FC

QUARTERLY PROGRESS REPORT

JULY 15, 1956

SOLID-STATE AND MOLECULAR THEORY GROUP
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS

QUARTERLY PROGRESS REPORT NO. 21

SOLID-STATE AND MOLECULAR THEORY GROUP

Massachusetts Institute of Technology
Cambridge, Massachusetts

O. N. R. Contract N5ori-07856

July 15, 1956

PERSONNEL

Faculty

Professor J. C. Slater, Director

Professor G. F. Koster (on leave of absence)

Staff Members, Research Assistants, and Graduate Students

H. A. Aghajanian

L. C. Allen

F. J. Corbató (in Professor Morse's group)

A. J. Freeman

L. P. Howland

A. R. Olson

M. M. Saffren

T. D. Schultz

R. E. Watson

J. H. Wood

Research Fellow

J. Hawgood

Staff Members, Lincoln Laboratory
(Air Force Contract No. AF 19(122-458)

A. M. Karo

R. K. Nesbet

Computers

Hannah Paul

I. Parkash

Secretary

Phyllis Fletcher

PUBLICATIONS

Quarterly Progress Reports Nos. 1-21, July 15, 1951 - July 15, 1956.

Technical Report No. 1, Ferroelectricity in the Ilmenite Structure, H. C. Schweinler, October 15, 1951.

Technical Report No. 2, Determination of the Dielectric Constant and Conductivity of Germanium by Microwave Methods, Hsi-Teh Hsieh, May 1, 1952.

Technical Report No. 3, Electronic Structure of Atoms and Molecules, J. C. Slater, February 15, 1953.

Technical Report No. 4, Electronic Structure of Solids I: The Energy Band Method, J. C. Slater, July 15, 1953.

Technical Report No. 5, Electronic Structure of Solids II: The Perturbed Periodic Lattice, J. C. Slater, December 15, 1953.

Technical Report No. 6, Electronic Structure of Solids III: Configuration Interaction in Solids, J. C. Slater, April 15, 1954.

Technical Report No. 7, Electronic Structure of Molecules. Some Recent Developments, Roy McWeeny, May 1, 1955.

Technical Report No. 8, Notes on Group Theory, G. F. Koster, March 1, 1956.

Journal Articles since July 1, 1955

F. J. Corbató, On the Computation of Auxiliary Functions for Two-Center Integrals by Means of a High-Speed Computer, J. Chem. Phys. 24, 452 (1956).

R. K. Nesbet, Configuration Interaction in Orbital Theories, Proc. Roy. Soc. (London) A230, 312 (1955).

R. K. Nesbet, Excited Electronic States of 1, 3-Butadiene, Proc. Roy. Soc. (London) A230, 322 (1955).

R. K. Nesbet, Localized Orbitals in Nuclear Structure, Phys. Rev. 100, 228 (1955).

TABLE OF CONTENTS

Quarterly Progress Report No. 21

on

Project N5ori-07856

SURVEY

Several major programs of calculation have been finished up during the period covered by this Report. Mr. Freeman, in the first place, has completed his calculation on the electronic energy of the OH molecule, and has fulfilled all the requirements for the doctor's degree. He leaves the group at the end of June. His calculations represent one of the few really complete treatments of a molecular wave function by configuration interaction; they are particularly valuable because he has carried through the work both using atomic orbitals, with complete treatment of the orthogonality problem, and using molecular orbitals. It is particularly interesting to compare his results on OH with the similar calculations of Scherr on N_2, of Sahni on BH, and of Karo and Olson on LiH; these represent most of the calculations of comparable rigor which have been carried through up to now. The striking result, a somewhat disconcerting one, is that the calculated binding energy forms a very different fraction of the experimental value for these various cases. One cannot, then, simply apply a fixed correction factor to the calculated values to get a correct value. Scherr and Freeman have both found quite small fractions of the experimental value, whereas Sahni and Karo and Olson have found a large fraction of the experimental value.

The conclusion which we must draw from this, I believe, is that further and much more extensive configuration interaction must be used, before one can get calculated results that can be trusted. It is well known that though the total energy of the separated atoms, or of the molecule, can be calculated with an error of only about half a percent by the methods we are now using, nevertheless this residual error in absolute magnitude is several times as large as the binding energy which we are seeking. We should have to get the total energy with an error of roughly a tenth as great as at present, before we could begin to trust the binding energy very seriously. The work which Nesbet and Watson have been doing on configuration interaction in helium, the work which I have been doing on that same problem (mentioned in the preceding Quarterly Progress Report), and similar work which Shull and Löwdin have been doing, all suggest that with a relatively simple configuration interaction one can decrease the error of the calculation of the helium atom to about ten percent of the error in the Hartree-Fock energy. A similar improvement is required to make the molecular calculations at all reliable, and we must look forward to similar configuration interactions there, as a goal to be attained as rapidly as possible.

The other two calculations which have been virtually completed are on energy

bands: Corbató's work on graphite, and Howland's on KCl. These have both been carried through by the tight binding method, including detailed calculation of the required many-center integrals, and both serve to mark a new advance in the use of the tight-binding method. Corbató, in his work on the σ as well as the π-bands in graphite, gives us a reliable estimate of the actual shape of the occupied energy bands for this important material. His results could be appreciably in error -- he has used an assumed periodic potential, without carrying through a self-consistent field calculation, and has merely found the one-electron energy in this periodic potential. Nevertheless his results are so reasonable that it seems likely that more accurate calculations, when they become possible, will merely verify the general correctness of his results.

Howland presents in this Progress Report a discussion of the lattice energy of KCl, but his calculations include much additional material, as well, including the details of the energy bands. These calculations represent a higher degree of sophistication than Corbató's, in that Howland has set up a determinantal wave function, and computed its energy, including all the various integrals. His values of lattice energy, which can be compared with Löwdin's earlier work, show that Löwdin omitted certain interactions which are of significant size. These calculations provide one of the most accurate results which have been obtained for the energy of a crystal lattice.

The reason why Howland was able to get more complete results than Corbató is based essentially on the difference between the two types of crystals. Graphite of course is a covalently bonded crystal, which means that the valence electrons of neighboring atoms have a very large overlap with each other. Potassium chloride, on the contrary, being an ionic crystal, has wave functions for the outer electrons which overlap only slightly, their overlap taking care of the repulsion between closed shells. It is this much smaller magnitude of the overlap in KCl which makes it inherently a simpler problem for the application of the tight-binding method, and which makes possible a higher degree of approximation than in graphite. A calculation of the order of difficulty which Corbató has carried through in graphite is a very major effort, which as far as we know has never been even approached in previous studies of covalently bonded crystals by the tight-binding method. Corbató considers that this method would prove to have very nearly insuperable difficulties for a crystal much more complicated than graphite; in this case he was greatly helped by the two-dimensional nature of the crystal, an almost unique property of graphite.

In addition to these calculations which have reached virtual completion, Schultz's considerations regarding the polaron have advanced a great deal in recent months, and he is bringing this work to a conclusion, hoping to finish it during the summer. The other work of the group is progressing well, and several other pieces of work should be brought to a conclusion before many more months.

J. C. Slater

1. MAGNETIC HYPERFINE STRUCTURE OF LITHIUM

A series of calculations have been carried out on the ^2S ground state of lithium by methods described earlier.[1] This is an attempt to obtain the mean value of the operator

$$f = \sum_{i=1}^{3} \frac{\delta(r_i)}{r_i^2} \sigma_{zi} .$$

The experimental value determined from the magnetic dipole hyperfine structure is $\langle f \rangle = 2.90\ a_o^{-3}$.

Configuration interaction calculations have been made using ^2S codetors (linear combinations of determinantal functions) constructed from analytic orbitals orthogonal to approximate self-consistent orbitals. Coefficients in the expansion of a set of orthonormal orbitals which includes the occupied self-consistent orbitals, constructed from a set of basic analytic orbitals, have been obtained by the Roothaan procedure,[2] under equivalence restriction. This means that the matrix equations of the Roothaan procedure are solved only for orbitals of positive spin; orbitals of negative spin are constrained to have spatial factors identical with the orbitals of positive spin. This introduces no approximation in a configuration interaction calculation so long as all configurations which can be constructed from the given set of basic orbitals are either included explicitly or are shown to have a negligible effect on the value of the quantity being calculated.

A preliminary calculation was made with five s-orbitals, three p-orbitals, and two d-orbitals. The calculated Hartree-Fock energy H_{oo} was - 7.43241 a.u. and the mean value of the hyperfine coupling operator f was $2.10759\ a_o^{-3}$ for a single determinant (Hartree-Fock approximation) and $2.66019\ a_o^{-3}$ after a configuration interaction calculation carried out by second order perturbation methods. The contribution of configurations including p- and d-orbitals to the final value of $\langle f \rangle$ was negligible. It was found that configurations which were most important in depressing the energy had little effect on $\langle f \rangle$ and vice versa. Since all coefficients of configurations affecting $\langle f \rangle$ were extremely small it does not seem likely that significant errors can be attributed to use of the perturbation method.

A series of calculations were done with six s-orbitals and no orbitals of higher angular momentum, with results as follows:

Calculation	Single determinant		Configuration interaction
	H_{oo}	$\langle f \rangle$	$\langle f \rangle$
2.	-7.43250 a.u.	$2.05565\ a_o^{-3}$	$2.66706\ a_o^{-3}$
3.	-7.43242	2.06220	2.61702
4.	-7.43259	2.11881	2.67834.

(MAGNETIC HYPERFINE STRUCTURE OF LITHIUM)

Although configuration interaction gives a marked improvement over the Hartree-Fock calculation of $\langle f \rangle$, the results appear to indicate a value of about 2.68 a_o^{-3} for this quantity which is insensitive to changes in the number of basic orbitals, for a wide range of values of the exponent of the sixth basic s-orbital. The first five orbitals were the same for all calculations. So far it has not been possible to account for the discrepancy between this result and the experimental value, $\langle f \rangle =$ 2.90 a_o^{-3}.

References

1. R. K. Nesbet, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., July 15, 1955, p. 27.

2. R. K. Nesbet, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., October 15, 1955, p. 4.

R. K. Nesbet

2. ATOMIC WAVE FUNCTIONS

The most recent calculation for He has given a result of -2.9010 a.u. This involves an SCF calculation with 4s like, 3p like, 2d like and 1f like basis orbitals,[1] followed by diagonalizing the 20 × 20 configuration interaction matrix.

Whirlwind has been used in two calculations on Fe. Nesbet's[1] programs have again been used, once on a $3d^6 4s^2$ configuration and once on a $3d^7 4s^1$ configuration. The principal problem has been that of establishing the rules for choosing the basis functions. To this purpose, several calculations were done on closed shell transition elements for which there are Hartree-Fock results. Good agreement with the H-F results was the principal criterion for the basis orbitals. A good choice of basis orbitals is very important, since the size of the computer limits the number which may be used. For example, we are using three basis functions for the Fe 3d orbitals. It appears that the best choice of basis functions in the closed shell case does not exactly interpolate to a best choice for the unfilled shell case and we are still in the process of forming the rules for these choices.

Reference

1. R. K. Nesbet, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., April 15, 1955, p. 38.

R. E. Watson

3. THE LITHIUM HYDRIDE MOLECULE

Calculations of the electronic energy for the ground state of lithium hydride by the self-consistent molecular orbital method are in progress. The electronic configuration of this state is represented as $(1\sigma)^2 (2\sigma)^2 \, {}^1\Sigma^+$. The binding energy has been obtained for five internuclear distances, and the results are given in Table 3-1.

Table 3-1

	Internuclear distance (atomic units)				
	2.0	2.6	3.0	3.5	4.0
SCF-MO Method:	+1.1413	-0.8702	-1.1989	-1.1464	-0.8371
Case 1:	+1.1019	-0.9310	-1.2794	-1.2912	-1.1072
Δ:	+0.0394	+0.0608	+0.0805	+0.1448	+0.2701

The molecular orbitals are found as a linear combination of the four atomic orbitals which we are using. An inspection of the coefficients of the atomic orbitals forming the molecular orbitals for internuclear distances near the equilibrium value indicates that the 1σ corresponds to a nearly pure lithium 1s orbital, and that the 2σ corresponds on the whole to a combination of the lithium 2s and hydrogen 1s orbitals, with a lesser mixing of the lithium 2p function. Therefore, it appears that an approximate comparison can be made with prior work (case 1 of the previous Progress Report) in which we excluded 2p orbitals in the configuration interaction problem. In Table we have given these results again and also the difference in the binding energy calculated by the two methods.

We may note that the single configuration molecular orbital treatment is becoming worse as the internuclear distance increases. Although we have only made a very preliminary analysis of the effects of configuration interaction, we should expect that the final result for the binding energy will be about that obtained for case 2 of the preceding Progress Report, and perhaps somewhat better since we have the additional mixing in of the 1s lithium function. Our previous work, however, has indicated that the inclusion of the 1s lithium electrons will be comparatively unimportant.

The four molecular orbitals which are constructed in the process of making the calculation are of σ symmetry (zero component of orbital angular momentum about the internuclear axis), since we have not as yet introduced the 2p(m = + 1) or the 2p(m = - 1) atomic orbitals into the calculation. It now seems that it would be of sufficient interest to include these 2p functions in both of the schemes which we are using. In the Löwdin formalism this would include an additional configuration to the six previously used and discussed as case 2.[1] The Roothaan method goes through straight-

forwardly with the proper listing of the additional integrals in the Whirlwind programs. The radial part of the integrations have already been performed so that only the angular factors need to be computed.

Computation of the integrals for the lithium hydride molecule at an internuclear distance of eight atomic units is very nearly completed. We have found that the convergence of hybrid and exchange integrals is slow, but still satisfactory even at this distance. The binding energy will be computed for this distance using the conventional configuration interaction scheme as well as the self-consistent molecular orbital procedure. Comparison of these results should prove interesting because of the failure of the ground state configuration molecular orbital treatment at larger internuclear distances.

Reference

1. A. M. Karo and A. R. Olson, Quarterly Progress Report, Solid-State and Molecular Theory Group, M. I. T., April 15, 1956, p. 17.

A. M. Karo and A. R. Olson

4. ELECTRONIC ENERGY OF THE OH MOLECULE

This is the final report under this title. The calculations described only briefly in previous reports have been completed and submitted as a thesis to the Physics Department. In conclusion, some of the more pertinent details omitted in previous contributions to these reports along with some of the results of the configuration interaction (CI) studies are presented here.

CI Calculation Using Non-Orthogonal AO's

Under this heading, we have described in previous reports, a CI study which used as basis those orbitals natural to the isolated atoms or AO's. The non-orthogonality of these AO's and of the various configurations formed from them was treated without approximation by the method of Löwdin. The necessary integrals involving the AO's were calculated using methods described previously. Table 4-1 lists the AO configurations of $^2\pi$ symmetry enumerated in a previous Report.[1] In this table s is the oxygen 1s function, S the oxygen 2s function, and p_o, p_+, p_- denote the three 2p orbitals in oxygen with components of angular momentum equal to respectively 0, +1, and -1. h denotes the hydrogen 1s state which is not made orthogonal to the oxygen orbitals.

Table 4-1
Enumeration of the AO configurations

State	Coefficient	s	S	h	p_o	p_+	p_-
Ψ_1	1	+-	+-	+-	+-	+	
Ψ_2	1	+-	+-	+-		+-	+
Ψ_3	1	+-	+-		+-	+-	+
Ψ_4	$1/\sqrt{2}$	+-	+-	+	-	+-	+
	$-1/\sqrt{2}$	+-	+-	-	+	+-	+
Ψ_5	$2/\sqrt{6}$	+-	+-	+	+	+-	-
	$-1/\sqrt{6}$	+-	+-	+	-	+-	+
	$-1/\sqrt{6}$	+-	+-	-	+	+-	+
Ψ_6	$1/\sqrt{2}$	+-	+	+-	-	+-	+
	$-1/\sqrt{2}$	+-	-	+-	+	+-	+
Ψ_7	$2/\sqrt{6}$	+-	+	+-	+	+-	-
	$-1/\sqrt{6}$	+-	+	+-	-	+-	+
	$-1/\sqrt{6}$	+-	-	+-	+	+-	+
Ψ_8	$1/\sqrt{2}$	+-	+	-	+-	+-	+
	$-1/\sqrt{2}$	+-	-	+	+-	+-	+
Ψ_9	$2/\sqrt{6}$	+-	+	+	+-	+-	-
	$-1/\sqrt{6}$	+-	+	-	+-	+-	+
	$-1/\sqrt{6}$	+-	-	+	+-	+-	+
Ψ_{10}	1	+-		+-	+-	+-	+

(+) and (-) denote the ordinary spin functions. Each row represents a single Slater determinant, a state being taken as a sum of rows with coefficients (given to the left of each row) which make these states eigenfunctions of the total spin operator.

In Table 4-2, the expansion coefficients, C_K, and the lowest root of the secular equation giving the binding energy, E_B, are listed both for the five configurations formed by keeping the 1s and 2s oxygen orbitals doubly filled, and for the more complete ten configuration treatment which results when the 2s electrons are excited. From Table 4-2 we observe that the three most important states are Ψ_3, Ψ_4 and Ψ_8; only Ψ_3 corresponds to a polar state OH^+.

None of the configurations have a diagonal energy lower than the total energy, E_∞, of the separated atoms; in particular, this is also true for the configurations Ψ_4 and Ψ_8 which correspond to valence bond states (since they describe bonds between the p_o and h and the S and h orbitals, respectively). A linear combination of these states, forming an s-p_o hybridized bond with the h function, still fails to give binding even though the coefficients are determined by a variational procedure. This is to be expected since the atoms in this hydride are fairly close together, and so are in that region in which the familiar Heitler-London approximation is least valid. Hence a description in terms of rigid AO's such as the ones employed here should be a poor approximation.

E_B = -. 0627 Rydbergs for the 5 × 5 matrix of interaction: the remaining five states succeed in lowering it to E_B = -. 0764 Rydbergs. Since the observed value is -. 337 Rydbergs (including the zero-point energy of . 017 Rydbergs) the ten configurations gives only 22 percent of the experimental value. (More will be said later about this result, when the MO scheme has been presented.) The total energy is of course in better percentage agreement with experiment yielding 99. 5 percent of the measured value. The lowering of the energy, brought about by those states formed by exciting the 2s electrons, is very small -- hardly justifying the amount of computational effort that was involved.

Table 4-2

Values of the expansion coefficients

States Ψ_1 through Ψ_5	States Ψ_1 through Ψ_{10}	
E_B = - . 0627 (Ryd.)	E_B = - . 0764 (Ryd.)	
c_1 = . 011209	c_1 = . 014767	c_6 = -. 005303
c_2 = . 016577	c_2 = . 017306	c_7 = -. 010048
c_3 = . 471287	c_3 = . 414435	c_8 = -. 122771
c_4 = . 626745	c_4 = . 607075	c_9 = -. 02605
c_5 = . 036056	c_5 = . 035611	c_{10} = -. 02723

Since this calculation is the first of its kind, comparison can be made only with the results obtained by other theoretical methods. In particular, since we have worked out the same problem by the MO-LCAO method, we have in essence built in our own check on the results just described.

CI Study Using MO LCAO's

In this scheme another configuration interaction calculation is carried out using as basis a set of orthonormal MO's which are determined from the same fixed set of AO's used in the last section. These MO's are determined by Roothaan's[2] SCF procedure for finding the "best" set of MO LCAO's which minimize the energy of a single configuration at each value of the internuclear separation. In this sense the MO's are not of the rigid form employed in the AO scheme. These SCF MO's will then be used as basis functions for a configuration interaction calculation of the molecular ground state. In contradistinction to the work presented in the previous section no elaborate formalism for handling the matrix elements is needed. The MO's form an orthonormal set and so none of the orthogonality difficulties encountered there appear in this study.

Determination of the "Best" Single Configuration MO's

The LCAO approximation constructs symmetry orbitals from a set of atomic functions. If we call the AO's ϕ_j, then the MO's, ψ_i, are chosen in the form

$$\psi_i = \sum_j C_{ij} \phi_j \qquad (4\text{-}1)$$

The C_{ij} are expansion coefficients, undetermined as yet. To satisfy the Pauli principle, we shall approximate the molecular state function by a single Slater determinant, Ψ_o, made up from the ψ_i as MO's. We want to determine that set of MO's which will give the lowest possible energy for Ψ_o subject to the restriction that the ψ_i's form an orthonormal set. These "best" MO's are determined by the Roothaan method which uses the variational procedure in a self-consistent way to select the coefficients, C_{ij}, which make Ψ_o stationary. Since Meckler and Nesbet have discussed their programs for Whirlwind for carrying out these computations in other issues of these Reports, we shall give no further details here.

For OH, from the six available atomic functions only the following twelve SCF LCAO MO's can be formed: 1σ, 2σ, 3σ, 4σ, π^+, π^- of plus spin and $\overline{1\sigma}$, $\overline{2\sigma}$, $\overline{3\sigma}$, $\overline{4\sigma}$, $\overline{\pi^+}$, $\overline{\pi^-}$, of minus spin. These symmetry MO's, as indicated by the notation, belong to irreducible representations of the group $C_{\infty v}$, the symmetry group of the molecule; the orbitals are labeled in the order of increasing energy. Since the OH molecule has an odd number of electrons in a non-closed shell ground state, the MO's

of different spin cannot be identical, and so must have different LCAO coefficients. This is due to the difference in exchange energy between those electrons having the same spin as the odd electron and those of opposite spin. The true solution of the H-F equations would therefore result in different sets of integro-differential equations for symmetry orbitals of opposite spin. Furthermore, the standard eigenvalue form of the H-F equations could no longer be retained. For these reasons we chose not to solve the more exact (and difficult) H-F equations for the MO's of both spins but arbitrarily define the LCAO MO's to be identical for electrons of either spin and solve the SCF equations for one spin set only. These approximate solutions of the (now modified) Roothaan procedure satisfy the equivalence restriction of Nesbet and are thus insured of forming an orthonormal set of symmetry orbitals with which to approximate the molecular ground state. While not exactly equivalent to the true solutions of the H-F equations (which we cannot find), our MO's should differ from these only in a negligible way.

The ground state configuration of OH (with $^2\pi$ symmetry) is taken to be

$$(1\sigma)^2\,(2\sigma)^2\,(3\sigma)^2\,(\pi^+)^2\,(\pi^-\alpha),\ \Psi_o \tag{4-2}$$

in which each of the MO's is doubly occupied except for the π^- orbital which alone has an unpaired (α) spin. The 4σ orbitals are not occupied in the ground state and so represent excited orbitals. The MO's expressed as LCAO's are simply written as

$$\begin{aligned} m\sigma &= C_{m_1}s + C_{m_2}S + C_{m_3}p_o + C_{m_4}h;\ m = 1, 2, 3, 4 \\ \pi^+ &= p_+ \\ \pi^- &= p_- \end{aligned} \tag{4-3}$$

The degenerate orbitals, π^+ and π^-, consisting of only one-member terms, have their LCAO coefficient uniquely determined by the normalization condition. The H-F equations thus reduce to a standard eigenvalue problem involving the solution of a 4×4 secular determinant for the LCAO MO's. Table 4-3 lists the computed coefficients for the SCF LCAO's along with the values of the orbital energies, ϵ_i, for three values of the internuclear distance. The inner-outer-shell mixing of the AO's is very small. The 1σ MO is made up almost purely from the s orbital (the oxygen atomic 1s function), the higher σ orbitals contain only a small contribution from this AO. The variation in charge distribution among the AO's is shown in Table 4-3 both as a function of internuclear distance and among the σ orbitals for a particular internuclear distance.

Table 4-3

MO	Internuclear Distance	ϵ_i	LCAO Coefficients s	S	p_o	h
1σ	1.8	-20.57499	+.99594	$+.84424 \times 10^{-2}$	-1.22191×10^{-3}	$+.58448 \times 10^{-2}$
	2.0	-20.57033	+.99730	$+.76574 \times 10^{-2}$	$-.8171 \times 10^{-3}$	$+.4638 \times 10^{-2}$
	2.2	-20.57466	+.99814	$+.71170 \times 10^{-2}$	$-.5205 \times 10^{-3}$	$+.3735 \times 10^{-2}$
2σ	1.8	- 1.34824	$+.50808 \times 10^{-2}$	+.89639	- .13903	- .14720
	2.0	- 1.384824	$+.21657 \times 10^{-2}$	+.92140	- .10329	- .13102
	2.2	- 1.32475	$-.1433 \times 10^{-3}$	+.94217	- .075819	- .113007
3σ	1.8	- .64544	-.029480	+.43225	+ .76471	+ .39694
	2.0	- .62173	-.026604	+.38501	+ .74848	+ .43635
	2.2	- .59637	-.023346	+.33659	+ .73721	+ .46590
4σ	1.8	+ .40964	-.087622	+.71603	- .84229	+1.28264
	2.0	+ .32234	-.066663	+.59240	- .82447	+1.18147
	2.2	+ .25289	-.051357	+.49272	- .80660	+1.10300
π	1.8	- .59927				
	2.0	- .59260	p_+ or p_-			
	2.2	- .58749				

Note: These one-electron energies are for the MO's with plus spin only. The MO's with negative spin have energies which differ from these by an exchange integral with the π^- electron. The unit of energy is 2 Rydbergs.

The total energy of the molecule is the sum of the nuclear repulsion energy and the one-electron energies of the occupied SCF LCAO's in the Ψ_0 configuration. The binding energy is calculated by subtracting the total energy of the free atoms from the value computed for the molecule. In Table 4-4, the results of these calculations are presented and compared with the corresponding experimental values. The total molecular energy is quite good whereas the binding energy seems a bit disappointing. Actually though, these values are consistent with the results of other SCF LCAO calculations. For comparison, we list in Table 4-5 the results of Sahni[3] on BH and Scherr[4] on N_2, the only other molecules reported to have been computed employing no approximations other than those inherent in the method. (The results of Karo and Olson on LiH discussed by them in this Report were not available when Table 4-5 was prepared and so could not be included therein.) Both authors used Slater AO's with Slater's values for the exponents; the energy was calculated at a value of the internuclear distance equal to the experimentally observed equilibrium value. The data for OH listed in Table 4-5 was calculated at the internuclear separation equal to 2.0. The total energy of the separated atoms for OH is seen to be better than for N_2 or BH. This is to be expected, since Hartree-Fock functions have more physical content as AO's than do the simple Slater functions. Correspondingly, the molecular energy also compares just as favorably. The magnitude of the binding energy is about the same for all three calculations. Sahni uses the value of 2.6 e.v. for the observed dissociation energy. Since Gaydon[5] actually recommends the value of $3.0 \pm .4$ e.v., both values were included in Table 4-5 to indicate the range of the probable binding energy which was obtained for BH. Sahni does not specifically say that he included a correction for the zero point vibration energy and so it is probably quite correct to assume that no such correction was made. If included, this would decrease his binding energy result, bringing it more in line with the other results quoted in Table 4-5b.

As a check on the stability of the binding energy with respect to changes in values of the integrals, the oxygen kinetic energy integrals were changed by as much as .04 Rydbergs. (These integrals were chosen because they represent the most inaccurate integrals calculated in this work.) The total energies of both the molecular and free atom systems changed, but the binding energy was almost completely unaffected.

CI Using SCF LCAO's

Having determined that set of LCAO MO's which gave the lowest energy of a single configuration, we are now in a position to study the effects of configuration interaction in further lowering the energy of the molecule. All possible configurations possessing the appropriate symmetry ($^2\pi$) are to be formed from the available

Table 4-4

Binding energy of OH

		Energy of separated atoms (Rydbergs)	Ratio of calculated to observed	Molecular energy (Rydbergs)	Ratio of calculated to observed	Binding energy		
						Rydbergs	e. v.	Percent of observed
Internuclear separation	1.8	-150.578	.9957	-150.640	.9939	-.062	.84	18.4
	2.0	-150.578	.9957	-150.650	.9940	-.072	.98	21.4
	2.2	-150.578	.9957	-150.563	.9934	-.069	.94	20.5
Experiment		-151.226		-151.563		-.337*	4.58	

*Includes zero point energy of .017 Rydbergs

Table 4-5a

Comparison of computed and observed total energies of N_2, BH and OH molecules

	Total energy of free atoms			Total energy for molecule		
	Computed (Rydbergs)	Observed (Rydbergs)	Ratio of computed to observed	Computed	Observed	Ratio
N_2	-217.060	-218.508	.9934	-108.574 (Ryd.)	-109.618 (Ryd.)	.9905
BH	- 50.122	- 50.503	.9925	-681.755 (e. v.)	-686.946 (e. v.)	.9925
OH	-150.578	-151.226	.9957	-150.650 (Ryd.)	-151.563 (Ryd.)	.9940

Table 4-5b

Comparison of computed and observed binding energies for N_2, BH and OH

	Computed	Observed	Ratio of computed to observed
N_2	-1.197 e. v.	-9.90 e. v.	12.1 percent
BH	-1.794 e. v.	-2.6 (-3.4) e. v.	70 percent (53 percent)
OH	- .98 e. v.	-4.58 e. v.	21.4 percent

LCAO MO's in Eq. (4-3). Since only the 4σ orbitals were not included in the Ψ_o configuration, the excited configurations, Ψ_K, are easily formed by promoting electrons from the lower lying occupied orbitals into the excited 4σ states. These are presented in Table 4-6 with the same notation as was used in Table 4-1. The Ψ_K are orthonormal since the orbitals are, and so the formulae for the matrix elements of the Hamiltonian between two Slater determinants are much simpler than for a non-orthogonal basis.

The CI problem is solved by diagonalizing the energy matrix (H_{KL}). Since there are 17 states made up from 23 Slater determinants, the computation of all the matrix elements between them is no small job. Fortunately, the simplifications cited by Nesbet[6] were used to reduce substantially the magnitude of the calculations.

According to Brillouin's theorem, the matrix elements of energy between determinants which differ by a single orbital are identically zero. Our set of LCAO MO's are solutions of the H-F equations, modified by the equivalence restriction. That is, for single substitutions of orbitals of plus spin Brillouin's theorem is automatically satisfied whereas the single substitution matrix elements involving orbitals of negative spin are not zero, but are found nevertheless to be very small. We need therefore only include those configurations which are formed by double substitution for those occupied orbitals in Ψ_o. This immediately eliminates the states Ψ_7 through Ψ_{10} inclusive from the configuration matrix.

The contributions of the excited configurations, Ψ_K, towards lowering the energy of Ψ_o, can at best be very small, since as we have seen, Ψ_o itself is a fairly good representation of the molecular ground state near the equilibrium internuclear distance. (CI effects become increasingly important with increasing internuclear distance because the MO's become an every poorer approximation as the molecular system approaches the free atom stage.) For this reason Nesbet[6] has proposed the use of second order perturbation theory for approximately diagonalizing the energy matrix. Using the familiar formulae of perturbation theory, the configurations Ψ_4, and Ψ_9 through Ψ_{16} must play a negligible role, since the 1σ state lies about 40 Rydbergs below the other one-electron states.

If the second order perturbation formula is used to diagonalize the secular equation the total energy (and hence the dissociation energy as well) is lowered by .0323 Rydbergs at the internuclear distance equal to 1.8 (which is the value used in the CI AO method described previously in the first section); the bordered determinant approximation* results in a similar lowering of .0320; the exact diagonalization of the 6×6 secular equation on Whirlwind gives a value of .0303 for the same quantity. Both the perturbation theory method and the bordered determinant method overestimate

*This method diagonalizes the matrix as approximated by the diagonal plus first column matrix elements.

Table 4-6
Enumeration of the MO configurations

State	Coefficient	1σ	2σ	3σ	π^+	π^-	4σ
Ψ_o	1	+-	+-	+-	+-	+	
Ψ_1	1	+-	+-		+-	+	+-
Ψ_2	1	+-		+-	+-	+	+-
Ψ_3	1	+-	+-	+-	+		+-
Ψ_4[a]	1		+-	+-	+-	+	+-
Ψ_5	$1/\sqrt{2}$	+-	+	-	+-	+	+-
	$-1/\sqrt{2}$	+-	-	+	+-	+	+-
Ψ_6	$2/\sqrt{6}$	+-	+	+	+-	-	+-
	$-1/\sqrt{6}$	+-	+	-	+-	+	+-
	$-1/\sqrt{6}$	+-	-	+	+-	+	+-
Ψ_7[b]	$1/\sqrt{2}$	+-	+-	+	+-	+	-
	$-1/\sqrt{2}$	+-	+-	-	+-	+	+
Ψ_8[b]	$2/\sqrt{6}$	+-	+-	+	+-	-	+
	$-1/\sqrt{6}$	+-	+-	+	+-	+	-
	$-1/\sqrt{6}$	+-	+-	-	+-	+	+
Ψ_9[b]	$1/\sqrt{2}$	+-	+	+-	+-	+	-
	$-1/\sqrt{2}$	+-	-	+-	+-	+	+

Table 4-6 (con'd)
Enumeration of the MO configurations

State	Coefficient	1σ	2σ	3σ	π^+	π^-	4σ
Ψ_{10} [b]	$2/\sqrt{6}$	+-	+	+-	+-	-	+
	$-1/\sqrt{6}$	+-	+	+-	+-	+	-
	$-1/\sqrt{6}$	+-	-	+-	+-	+	+
Ψ_{11} [a]	$1/\sqrt{2}$	+	+-	+-	+-	+	-
	$-1/\sqrt{2}$	-	+-	+-	+-	+	+
Ψ_{12} [a]	$2/\sqrt{6}$	+	+-	+-	+-	-	+
	$-1/\sqrt{6}$	+	+-	+-	+-	+	-
	$-1/\sqrt{6}$	-	+-	+-	+-	+	+
Ψ_{13} [a]	$1/\sqrt{2}$	+	+-	-	+-	+	+-
	$-1/\sqrt{2}$	-	+-	+	+-	+	+-
Ψ_{14} [a]	$2/\sqrt{6}$	+	+-	+	+-	-	+-
	$-1/\sqrt{6}$	+	+-	-	+-	+	+-
	$-1/\sqrt{6}$	-	+-	+	+-	+	+-
Ψ_{15} [a]	$1/\sqrt{2}$	+	-	+-	+-	+	+-
	$-1/\sqrt{2}$	-	+	+-	+-	+	+-
Ψ_{16} [a]	$2/\sqrt{6}$	+	+	+-	+-	-	+-
	$-1/\sqrt{6}$	+	-	+-	+-	+	+-
	$-1/\sqrt{6}$	-	+	+-	+-	+	+-

a. Negligible by second-order perturbation theory.
b. Negligible by Brillouin's theorem.

the CI and so where possible exact diagonalization of the secular equation is preferred.

The result then of solving the CI problem in terms of the MO LCAO's as basis is to give a value of the binding energy equal to -. 092 Rydbergs. This compares well with the value of -. 0764 Rydbergs reported for the AO scheme in the first section. This comparison can only be made at the nuclear separation, R, equal to 1. 8 at which the AO calculation was carried out. The minimum of energy for the single determinant approximation (see Table 4-4) occurs at R = 2. 05 atomic units which is some ten percent larger than the observed value of 1. 834 a. u. This result indicates that had the CI calculation of the first section been carried out at a value of nuclear separation larger than the value actually used, we would certainly have obtained a lower binding energy than was actually found.

Since the set of MO's is formed from the basic set of atomic orbitals, the same subspace of Hilbert space is spanned by both sets. If all possible configurations were formed from either set, the n-electron system would be equivalently described by both.[7] Neither would form a more complete description than the other and so the same energy levels would be derived from each.

The two calculations described cannot give the same results because the CI expansions are not equivalent. The configurations formed from the AO's as basis (see Table 4-1) did not include those states which resulted from exciting the oxygen 1s electrons into higher lying states. The CI calculation involving the SCF LCAO's, expanded the total wave function as a linear combination of all the configurations which could be obtained from the basic set of MO's. True, the configurations resulting from exciting 1σ electrons into higher orbitals were found to come into the expansion with extremely small coefficients and so were completely left out of the secular determinant. But the other σ orbitals each contain a small amount of the 1s oxygen AO, and so the configurations already contain a small but appreciable contribution from the 1s states. If there were no mixing in the LCAO's between the s orbital and the other spherically symmetric AO's, or if all the AO configurations were used, the two solutions would then agree. The value of -. 0764 Rydbergs obtained for the binding energy by the AO CI scheme is only . 016 Rydbergs above the result of the SCF LCAO configuration interaction calculation. This seems to be a reasonable amount to attribute to the CI lowering which would be introduced by those (seven) configurations neglected in the AO scheme. It may therefore be concluded that the results are consistent among themselves and seem to indicate a fair degree of numerical accuracy.

Conclusions

The results of the CI studies are not as good as we would like them to be. For closer agreement with experiment we should set up a more unrestricted CI

calculation by expanding the basic set of functions, mixing in (say) AO's with higher orbital angular momentum to provide the possibility of increased angular correlation.[8] Such an expanded CI calculation would completely alter the character of the problem we have completed here. There are no other Hartree-Fock orbitals for atomic oxygen available with which to augment the set used here. If more orbitals are to be introduced, it would be best to choose an entirely new set for the atom, so chosen as to provide the maximum degree of correlation.

The major inadequacy of the calculation lies in what seems to be a poor description of the π electrons. This is most easily seen in the MO picture where the π electrons are described by one-electron functions which are identical to the p_+ and p_- oxygen orbitals. In the molecular environment this picture of the outer electrons cannot be right. The complete localization of the π electrons around the oxygen center is correct only at infinite separation. In the molecular environment some of the π-electron charge clouds must be described by functions which spend an appreciable time near the hydrogen center. Our description cannot do this, since we are using a restricted set of AO's. We are again forced to conclude that in order to improve our results we must expand our basic set as outlined above.

Acknowledgments

I am happy to acknowledge the many ways in which past and present members of the Group, by their friendship and guidance, contributed to my education and to the completion of this problem. In particular, many thanks are due Professor J. C. Slater for his kind patience, his unfailing interest and constant encouragement during the time I was privileged to spend under his guidance.

Thanks are due Dr. R. K. Nesbet for keen advice regarding the Roothaan procedure, and for making available (and comprehensible) his programs for Whirlwind; F. J. Corbató for much help with his integration programs and techniques, without which the calculations would have been hopelessly difficult; Mrs. F. Abrams and Mrs. E. Mack for their painstaking care with the more tedious numerical computations; Mr. I. Prakash for his assistance with some of the hand calculations; and to Professor G. F. Koster for suggesting part of the problem and for his initial encouragement with it.

References

1. A. J. Freeman, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., January 15, 1956, p. 13.
2. C. C. J. Roothaan, Revs. Modern Phys. 23, 69 (1951).
3. R. C. Sahni, Scientific Report No. 22, University of Western Ontario, October 1, 1955.

References (con'd)

4. C. W. Scherr, J. Chem. Phys. 23, 569 (1955).

5. A. G. Gaydon, Dissociation Energies, Chapman and Hall, Ltd. 1947, p. 205.

6. R. K. Nesbet, Proc. Roy. Soc. (London) A230, 312 (1955) and Quarterly Progress Report, Solid-State and Molecular Theory Group, M. I. T., January 15, 1955, p. 18.

7. For a proof of this theorem, see A. Meckler, J. Chem. Phys. 21, 1750 (1953).

8. Similar to the calculations currently being carried out by Professor Slater (see Survey of last Quarterly Progress Report (April 15, 1956), H. Shull and P. O. Löwdin, J. Chem. Phys. 23, 1362 (L) (1955) and R. Watson, Quarterly Progress Report, Solid-State and Molecular Theory Group, M. I. T. April 15, 1956, p. 16.

A. J. Freeman

5. GROUND STATE OF THE HYDROGEN MOLECULE

The exchange and hybrid integrals which were evaluated by Merryman's program were found to be inaccurate for interatomic separation of one and two atomic units. These integrals are now being recalculated by the method of expansion about another center which is programmed for Whirlwind by F. J. Corbató.[1] Expansion of the exchange integrals gives infinite series which converge rapidly for all the required integrals. For the internuclear distance of one atomic unit it was found that, in all cases, seven terms of the series gave accuracy of six figures. The combination of terms in the series was done on Whirlwind by a program written by L. P. Howland. The Whirlwind time for evaluation of the final integrals averaged about 70 seconds per integral.

Reference

1. F. J. Corbató, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., April 15, 1955, p. 44.

H. A. Aghajanian

6. POLARIZATION EFFECTS IN THE FLUORINE ION

The numerical integration of the equations for our perturbed functions $v_{\ell \to \ell''}$ still show considerable sensitivity to the smoothness of the potential and the mesh size. However, for the uniform field case we have obtained a complete check on the perturbed functions of d-like symmetry and considerable improvement in the p and s-like ones. Also, we have recently obtained the v function of d symmetry for the dipole term of a point charge perturbing potential at a finite distance, R, from the origin. For R = 1.76 atomic units the v function for Neon has a behavior near the origin very similar to the corresponding uniform field (R = ∞) case and a maximum at approximately r = R.

Because of the delays and difficulties in obtaining our distorted functions by direct integration we have undertaken a calculation for the HF molecule based on a small set of unperturbed functions to describe the F^- ion and including a single d-like distorted function. This d function has been chosen to have a maximum very close to the position of the H^+ point charge. For the unperturbed functions the 1s is F. W. Brown's fit of his Hartree-Fock F^- calculation, the 2s is the single Slater atomic orbital which most nearly fits Brown's 2s function when orthogonalized to the 1s, and a single Slater AO was used for the 2p with the exponent of the exponential chosen so the AO has the same maximum as the Hartree-Fock function. Explicitly the radial parts of the 1s, 2s, 2p, d-distorted functions are: $e^{-8.75r}$, $re^{-2.40r}$, $re^{-2.67r}$, and $r^2e^{-2.00r}$, respectively.

We have obtained all of the necessary atomic and potential integrals from R. K. Nesbet's Whirlwind program (described by the writer and R. K. Nesbet in previous Progress Reports). These have been combined with the appropriate coefficients and classified in terms of the molecular symmetry. That is, the axis of quantization for the atomic functions is chosen as the internuclear axis allowing the atomic quantum number m_ℓ to go directly into the corresponding molecular quantum number with the combining coefficients the $C^k(\ell m_\ell, \ell' m_{\ell'})$'s tabulated by Condon and Shortley.[1] Using these integrals the parameter tapes for the Whirlwind program of the Roothaan scheme are being prepared.

Reference

1. E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra, Cambridge University Press, 1953, p. 178.

L. C. Allen

7. ENERGY BANDS OF GRAPHITE

The computation of energy bands in a two-dimensional model of graphite by means of the tight-binding method has been completed. Current effort is being devoted to the thesis write-up of this work. Thus, the following report is only a brief resume of the basis of the calculation and the major results which were obtained.

The graphite energy band calculations were carried out assuming a structure of an infinite two-dimensional hexagonal lattice of Carbon atoms. The atomic orbitals used to make up the one-electron Bloch waves were the Hartree-Fock atomic orbitals of the ground state neutral Carbon ^3P configuration calculated by Jucys.[1] The 1s and 2p orbitals were each fitted by a linear combination of three corresponding analytic Slater atomic orbitals, and the noded 2s orbital was fitted by a sum of three 1s and three 2s Slater atomic orbitals.[2] The fits were of high accuracy and were made for ease in the calculation of the many integrals. In the sense that the energy band calculation made was a one-electron approximation, it was necessary to choose an effective potential for the crystal. The crystal potential was taken to be a superposition of spherically symmetric atomic potentials. The atomic potential in turn was assumed to be the Coulombic potential arising from the effective nuclear charge function, $Z_p(r)$, centered on the atomic nucleus. The Z_p function for the ^3P configuration has been calculated by Freeman,[3] and it was because of this convenience that the particular configuration of Carbon chosen was used, since it was not felt that the current knowledge of energy band solutions gave any other conclusive choice. For computational convenience, the Z_p function was also fitted, a linear combination of four exponentials being used.

All the one-electron, two-center integrals (overlap, kinetic energy and potential) were done by the use of the usual prolate spheroidal coordinate analytic integration techniques suitable for Slater atomic orbitals.[4] Thus, these integrals required the evaluation of auxiliary functions[5, 6] followed by combinations of many terms. All the one-electron, three-center potential integrals (and also the two-center potential integrals) were evaluated by the spherical coordinate expansion-about-another-center technique, similar to that used by Löwdin,[7] and Barnett and Coulson,[8] which was described extensively in a previous Report.[9]

It is perhaps illuminating to give some of the computational perspective involved in the overall calculation. Inasmuch as the magnitude of numerical work involved was such that accuracy would have been difficult to maintain in any hand calculation, most of the computational work was done on the high-speed electronic computer Whirlwind I. The nearly total mechanization of the problem, although eliminating almost entirely any possible random mistakes, had the disadvantage of tending to obscure possible systematic mistakes. The latter shift of emphasis is one of the principle reasons that make the programming of a computer a non-trivial affair. A consequence is that logical simplicity of the computational procedure becomes a goal which is often

opposition to computational efficiency. There is also a great deal of difficulty in devising adequate test procedures for computer programs, since of necessity they must be tailored to the program itself. The ability of a programmer to cope with these computer problems develops mostly with experience. A large fraction of the time spent on the present calculation was thus used learning how to obtain the full potentiality of a high-speed computer.

In carrying out the calculation, the work fell into stages for each of which special computer programs were written. These were: a program for the semi-automatic fitting of the atomic orbitals and the Z_p function;[2] a program for generating the two-center integral auxiliary functions and then automatically combining terms to give the integrals between Hartree-Fock orbitals;[5] a program for generating the atomic orbital expansion functions necessary for the three-center potential integrals;[9] a program for performing the basic numerical quadratures of the three-center potential integrals;[9] and a requantization and summation program for forming the appropriate three-center integrals from the basic numerical quadratures.[9] The foregoing computer programs were sufficient machinery to prepare the basic two-center Hamiltonian and overlap integrals which served as input for the final master program which performed the energy band calculation. Explicitly the basic two-center integrals were of the form

$$\mathcal{M}_{ij}(\vec{\rho}_a) = \int \psi_i^*(\vec{r} - \vec{\rho}_a)\mathcal{M}(\vec{r})\,\psi_j(\vec{r})\,d\tau \tag{7-1}$$

where the ψ are atomic orbitals, $\vec{\rho}_a$ is the neighbor-vector, and

$$\mathcal{M}(\vec{r}) = \begin{cases} \mathcal{S}(\vec{r}) = 1, & \text{(overlap)} \\ \mathcal{H}(\vec{r}) = -\frac{1}{2}\nabla^2 - \sum_{\vec{\rho}_b} \dfrac{Z_p(\vec{r} - \vec{\rho}_b)}{|\vec{r} - \vec{\rho}_b|}, & \text{(Hamiltonian)} \end{cases} \tag{7-2}$$

the sum in the potential term being over all neighbor-vectors. In the present calculation, the three-center potential terms were neglected when $|\vec{\rho}_b|$ or $|\vec{\rho}_b - \vec{\rho}_a|$ exceeded the fourth neighbor-distance in the sum over $\vec{\rho}_b$.

The operation of the master energy band program then proceeded as follows. For a given value of the reduced wave vector, $\vec{k}$, the program computed the Hamiltonian and overlap matrix elements arising from the Bloch waves constructed from the atomic orbitals. These matrix elements were made real by taking judicious linear combinations of the Bloch waves as basis states, and had the form

$$M_{ij}(\vec{k}) = \sum_{\vec{\rho}_a} \pm \mathcal{M}_{ij}(\vec{\rho}_a) \begin{cases} \cos(\vec{k} \cdot \vec{\rho}_a) \\ \sin(\vec{k} \cdot \vec{\rho}_a) \end{cases} \tag{7-3}$$

where the terms in which $\vec{\rho}_a$ exceeded the ninth neighbor-distance were neglected. The program next solved the usual variationally-derived secular equation of the form

$$\sum_j H_{ij}(\vec{k})\, V_{jk}(\vec{k}) = E_i(\vec{k}) \sum_j S_{ij}(\vec{k})\, V_{jk}(\vec{k}) \tag{7-4}$$

and stored for later use the eigenvalues $E_i(\vec{k})$. A new value of the wave vector was then selected and the generation and solution of the secular equation repeated until the pre-set values of the wave vector were exhausted. Finally for convenience, the program displayed graphically on a photographic oscilloscope cross-sectional views of the energy bands, $E_i(\vec{k})$ vs $\vec{k}$, for values of the wave vector along the edges of a basic non-repeating 30^o-60^o-90^o triangle of the first Brillouin zone.

As has been implied, the secular equation which was considered had as basis states linear combinations of the ten one-electron Bloch waves formed from the 1s, 2s, and 2p atomic orbitals on each of the two atomic sites in the spatial unit cell. Because of the reflection symmetry in the Hamiltonian operator of the two-dimensional graphite lattice, the secular equation one obtains from these ten states immediately factors into two independent equations, one of order eight arising from reflection symmetric Bloch waves (σ states), and the other of order two from reflection anti-symmetric Bloch waves (π states). Thus the master computer program was arranged to independently calculate the energy band solutions arising from each of these secular equations, but the final results were graphically superimposed.

The major physical significance in a two-dimensional energy band calculation of graphite is the size of the gap between the five lowest (occupied) and the higher (excited) σ bands, and in particular whether or not the two lower π bands (valence and conduction) which are degenerate at one value of the wave vector, have their point of degeneracy in the σ band gap. If such a σ band gap is large enough to include all of the π bands, then it follows that a reasonable approximation for computing the conduction properties of a three-dimensional graphite would be to ignore the σ states; in the three-dimensional crystal the σ and π Bloch waves of alternate graphite layers interact, but the terminology is still used. Starting from the original work of Wallace,[10] this approximation has been the basis of all graphite energy band calculations with the exception of Lomer who has also considered two-dimensional graphite with σ bands.[11] As will be seen later, the numerical work of Lomer is believed to have a very serious approximation.

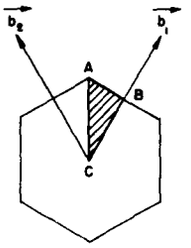

Fig. 7-1

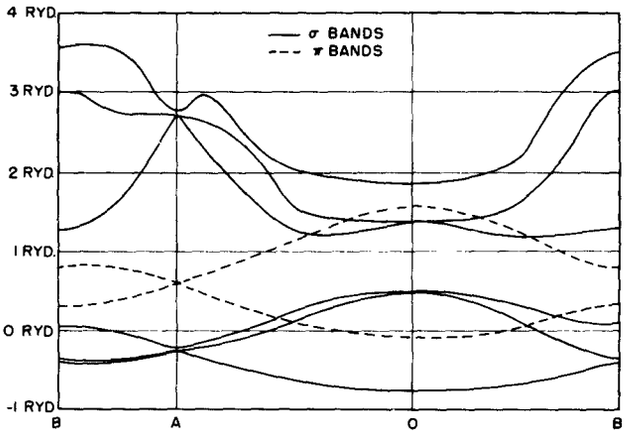

Fig. 7-2

The energy band solution of the present calculation is shown in Fig. 7-2 where the horizontal dimensions are the edges of the basic triangle of the first Brillouin zone as shown in Fig. 7-1. Energy values of interior points of the triangle were also found, but for brevity these values are not given here since it was found that the interior energy bands vary smoothly from the edge band values. Furthermore, the two lowest σ bands arising almost entirely from the 1s Bloch waves, are omitted from Fig. 7-2 since the bands are nearly independent of the wave vector and at an average value of -15.75 Rydbergs. It is observed that the highest occupied point in the σ bands occurs at pt. 0, ($\vec{k} = 0$), with a value of +.430 Rydbergs. The lowest excited σ band has roughly a constant minimum value for wave vector values forming an approximate circle about pt. 0, the minimum value being about +1.158 Rydbergs. The degeneracy point of the π bands falls at +.570 Rydbergs, a value representing the Fermi level for zero temperature. Thus, it is clear that these results support to some extent the usual approximation of neglecting the σ states in calculations of graphite conduction properties. Moreover, this calculation shows by virtue of the overlapping of the σ and π bands that for a cohesive energy calculation, which depends on energy values for all wave vectors of the Brillouin zone, the σ states must be included.

Consideration can also be made of the potential function used in the present calculation. The potential, which was formed by superposition of the Z_p function, clearly omits exchange effects. Slater has given a procedure for introducing an approximate exchange potential correction within the framework of the one-electron approximation.[12] This exchange potential correction, if applied, would be proportional to the cube root of the charge density of the occupied crystal wave functions.

Consequently, one would expect the occupied bands to be lowered more in energy than the unoccupied bands, since the unoccupied wave functions are orthogonal to the occupied wave functions. Thus, it is plausible that a more careful consideration of exchange effects in the present calculation would only broaden the σ band energy gap and would leave the present results qualitatively unchanged.

One of the more striking features of the present results is the smoothness of the energy bands. In fact, these bands are similar to those obtained from the Slater and Koster interpolation procedure wherein the tight-binding method is used with neglect of all but a few nearest-neighbor integrals.[13] It is therefore of interest to examine the stability of the present results in view of the several possible simplifying approximations.

Omission of the 1s Bloch waves was found to have an overall lowering and warping effect on the σ bands in such a way that the σ band gap was roughly reduced by half. Thus, the often-recognized importance of orthogonality is again emphasized. A second possible approximation made was the omission of all the three-center potential integrals. This left the π bands nearly the same but made a very pronounced change in the σ bands, again closing the σ band gap down to about half, but also lowering the gap so far that the π band Fermi level no longer was included.

Finally, the solutions were examined with respect to the approximation of omitting the higher neighbor integrals. The stable solution, which included up to ninth neighbor integrals, was found to be only slightly warped when only up to fifth neighbor integrals were included in the σ bands and when only up to third neighbor integrals were included in the π bands. However, further truncation of the neighbor integrals of the σ bands caused violent changes. (It is for this reason that the calculation made by Lomer, which included only first neighbor integrals, is not believed to be valid.) In addition, the effects of truncating only Hamiltonian or only overlap neighbor integrals were investigated. It was found that the solution was sensitive to both Hamiltonian and overlap neighbor truncation to roughly the same extent and that the two effects were essentially additive.

Thus, the results of all the approximation tests indicate clearly that the tight-binding method when used in a non-empirical way must be carried out with considerable mathematical rigor in order that a meaningful solution will be obtained.

References

1. A. Jucys, Proc. Roy. Soc. (London) A173, 59 (1939).
2. F. J. Corbató, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., October 15, 1954, p. 28.
3. A. J. Freeman, Phys. Rev. 91, 1410 (1953).
4. R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, J. Chem. Phys. 17, 1248 (1949).

References (con'd)

5. F. J. Corbató, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., July 15, 1954, p. 49.
6. F. J. Corbató, J. Chem. Phys. 24, 452 (1956).
7. P. O. Löwdin, Ph.D. Thesis, Uppsala (1948).
8. M. P. Barnett and C. A. Coulson, Phil. Trans. A243, 221 (1951).
9. F. J. Corbató, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., April 15, 1956, p. 33.
10. P. R. Wallace, Phys. Rev. 71, 622 (1947).
11. W. M. Lomer, Proc. Roy. Soc. A227, 330 (1955).
12. J. C. Slater, Phys. Rev. 81, 385 (1951).
13. J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).

F. J. Corbató

8. LATTICE ENERGY OF POTASSIUM CHLORIDE

The lattice energy of potassium chloride has been calculated in conjunction with a study of the electronic structure of the perfect and almost perfect crystal.[1] Lattice energy is the energy of the crystal relative to the energy of its separated ions; its negative is the cohesive energy. The present calculation is modeled directly after the comprehensive energy calculations of Dr. P. O. Löwdin.[2] In the present work, however, interactions between nearest chlorine ions (second neighbors in the lattice) have been included along with those between nearest neighbor potassium and chlorine ions; Löwdin limited himself to the latter. One purpose of doing the new calculation is to determine the contribution to lattice energy of these second neighbor interactions.

A further purpose of the new calculation is to provide checks on quantities which are being used in my study of electronic structure. For this reason my equations for contributions to lattice energy are written as far as possible in terms of quantities used directly in the electronic structure work. Term-by-term comparison with the calculations of Löwdin and with calculations based on the empirical Born-Mayer model will provide the check on these quantities.

Equations for Lattice Energy

The discussion below follows closely that given by Löwdin in his thesis,[2] and in general the notation is his.

Consider a perfect, infinite crystal of potassium chloride with its ions fixed and in its ground state. The crystal is divided into large identical regions, a particular region being symbolized by R. Let there be N unit cells and a total of 2M electrons in the region R. We take as a ground-state, many-electron wave function a single determinant $\Psi(1, 2 \ldots 2M)$ made up of M orthonormal space orbitals $\psi_i(j)$, each being doubly occupied; thus we take

$$\Psi(1, 2 \ldots 2M) = \left[(2M)!\right]^{-1/2} \det \left\{\psi_i(j)\ \eta(n)\right\}, \tag{8-1}$$

where $\eta(j)$ stands for one of the spin functions, $\alpha(j)$ or $\beta(j)$, and both occur for each i. This definition leads to the normalization integral

$$\int_R \Psi^*(1, 2 \ldots 2M)\, \Psi(1, 2 \ldots 2M)\, d\tau_1 \ldots d\tau_{2M} = 1. \tag{8-2}$$

Use of the symbol $d\tau$ in (8-2) is meant to imply spin summation as well as integration; use of dv will mean integration over space only.

With the above definitions the total energy of the crystal becomes

$$E_T = \frac{1}{N} \int_R \Psi^*\, H\, \Psi\, d\tau_1 \ldots d\tau_{2M}. \tag{8-3}$$

Here H is the crystal Hamiltonian, which we take to be as follows

$$H = \sum_{j=1}^{2M} H_j + \sum_{i,j=1}^{2M} G_{ij} + W, \tag{8-4}$$

In (8-4)

$$H_j = -\nabla_j^2 - \sum_{1}^{2N} (\text{sites } g) \frac{2Z_g}{r_{jg}}, \quad G_{ij} = \frac{2}{r_{ij}}, \quad W = \sum_{g,g'=1}^{M}{}' \frac{2Z_g Z_{g'}}{r_{gg'}}.$$

The letter g is used to identify sites, and Z_g is the nuclear charge on site g; energies are in Rydbergs and distances in atomic units. Substituting this Hamiltonian in Eq. (8-3), the total energy becomes

$$E_T = \frac{1}{N}\left\{W + 2\sum_{i=1}^{M}(H|ii) + \sum_{i,j=1}^{M}\left[2(G|ii|jj) - (G|ij|ji)\right]\right\}, \tag{8-5}$$

where $(H|ii) = \int \psi_i^*(1)\, H_1\, \psi_i(1)\, dv_1$, and $(G|ij|k\ell) = \int \psi_i^*(1)\, \psi_j(1)\, \frac{2}{r_{12}}\, \psi_k^*(2)\, \psi_\ell(2)\, dv_1\, dv_2$.

We now choose to construct the orthonormal orbitals $\psi_i(j)$ by making linear combinations of the M normally-occupied, free-ion, Hartree-Fock space orbitals $u_m(j)$, centered on appropriate sites in the crystal. Thus we write $\psi_i(j)$ as follows:

$$\psi_i(j) = \sum_{m=1}^{M} a_{mi}\, u_m(j), \quad i = 1 \ldots M. \tag{8-6}$$

The indices m, n, p and q will be reserved for identifying free-ion orbitals. With this equation for $\psi_i(j)$, Eq. (8-5) becomes

$$E_T = \frac{W}{N} + \sum_{m,n=1}^{M}\left[\sum_{i=1}^{M} a_{mi}^* a_{ni}\right]\left\{2(H|mn) + \sum_{p,q=1}^{M}\left[\sum_{j=1}^{M} a_{pj}^* a_{qj}\right]\left[(G|mn|pq) - (G|mq|pn)\right]\right\} \tag{8-7}$$

Eq. (8-6) relating the ψ's to the u's can be rewritten as a matrix operation on vectors in the form

$$\vec{\Psi} = \vec{U}A, \tag{8-8}$$

where $\vec{\Psi}$ and $\vec{U}$ are M-dimensional column vectors of the functions ψ_i and u_m respectively, and A is the M × M matrix of coefficients a_{mi}.

Let us define an M × M overlap matrix Δ for the free-ion orbitals by the following equation:

$$\Delta = \det \left\{\Delta_{mn}\right\},\ m = 1 \ldots M,\ n = 1 \ldots M, \tag{8-9}$$

where $\Delta_{mn} = \int_R u_m^*(1)\, u_n(1)\, dv_1$. Let us also define

$$S = \Delta - 1\ ,\ \text{or}\ S_{mn} = \Delta_{mn} - \delta_{mn}\ . \tag{8-10}$$

The corresponding overlap matrix for the ψ's is the $M \times M$ unit matrix. With these definitions the orthonormality of the ψ's is expressed by the matrix equation

$$1 = A^\dagger \Delta A, \tag{8-11}$$

where $A^\dagger$ is the adjoint of A. Since A is non-singular it has an inverse A^{-1}. Similarly Δ has an inverse Δ^{-1}. Multiplying Eq. (8-11) from the right by $A^{-1}\,\Delta^{-1}$ and from the left by A, (8-11) becomes

$$AA^\dagger = \Delta^{-1}\ , \tag{8-12}$$

$$\text{or}\ \sum_{i=1}^{M} a_{ni}\, a_{mi}^* = \Delta_{nm}^{-1}\ . \tag{8-13}$$

These equations must hold whether ψ is a Bloch function or a Wannier function or a Löwdin orthonormal function or whatever. They follow simply from the fact that we are constructing M orthonormal functions ψ from M linearly independent functions u. The identity of Eq. (8-13) simplifies the equation for total energy, Eq. (8-7), and the latter now becomes

$$E_T = \frac{W}{N} + \sum_{m,n=1}^{M} \Delta_{nm}^{-1} \left\{2(H|mn) + \sum_{p,q=1}^{M} \Delta_{qp}^{-1}\left[2(G|mn|pq) - (G|mq|pn)\right]\right\}\ . \tag{8-14}$$

To obtain the lattice energy from E_T we must subtract the total energy per unit cell of a crystal with an infinite interionic distance; the latter energy we call E_∞. Since the orbitals $u_m(j)$ are free-ion Hartree-Fock orbitals the consistent definition of this energy of the separated ions is

$$E_\infty = \frac{1}{N} \sum_g \left\{2 \sum_m {}^g(H^g|mm) + \sum_m {}^g \sum_p {}^{\bar{g}} \left[2(G|mm|pp) - (G|mp|pm)\right]\right\} \tag{8-15}$$

where $H^g = -\nabla^2 - 2Z_g/r_g$; we use Löwdin's convention that $\sum_m {}^g$ means a sum over orbitals u_m on site g, while $\sum_m {}^{\bar{g}}$ will mean a sum over orbitals on all sites in R except site g. In order to allow explicit subtraction of E_∞ from E_T, we define

$$\Delta_{nm}^{-1} = \delta_{nm} + P_{nm}\ . \tag{8-16}$$

Using Eqs. (8-14), (8-15), and (8-16) we can now write out equations for the crystal energy, thus;

$$E = E_T - E_\infty = E_{elstat} + E_{ex} + E_S, \tag{8-17}$$

where

$$\begin{aligned} E_{elstat} &= \frac{W}{N} + \frac{1}{N} \sum_g \left[2 \sum_m^g \sum_{g' \neq g} \left(- \frac{2Z_{g'}}{r_{1g'}} | mm \right) + \sum_m^g \sum_p^g 2(G|mm|pp) \right] \\ E_{ex} &= \frac{1}{N} \sum_g \left[- \sum_m^g \sum_p^g (G|mp|pm) \right], \text{ and} \\ E_S &= \frac{1}{N} \sum_g \sum_m^g \sum_n P_{nm} \left\{ 2(H|mn) + \sum_{pq} P_{qp} \left[2(G|mn|pq) - (G|mq|pn) \right] \right. \\ &\quad \left. + 2 \sum_p \left[2(G|mn|pp) - (G|mp|pn) \right] \right\}. \end{aligned} \tag{8-18}$$

This separation into the three terms of Eqs. (8-18) follows Löwdin's procedure; E_{elstat} is made up entirely of electrostatic interaction energies, E_{ex} is a crystal exchange contribution, and E_S is a contribution depending on free-ion overlap.

Electrostatic Energy

The electrostatic term in (8-18), E_{elstat}, can be rewritten in a more obvious form. Using the definition of W from (8-4), we can write

$$E_{elstat} = \frac{1}{N} \frac{1}{2} \sum_g \sum_{g' \neq g} \int \frac{2\rho_g(1)\, \rho_{g'}(2)}{r_{12}} \, dv_1 \, dv_2, \tag{8-19}$$

where

$$\rho_g(1) = Z_g \, \delta(\vec{r}_1, 0) - 2 \sum_m^g u_m^*(1) \, u_m(1).$$

This quantity, $\rho_g(1)$, is the charge density of a free Hartree-Fock ion at site g, including its nuclear "charge density". E_{elstat} is therefore the Coulomb energy of interaction of Hartree-Fock ions superposed to form a crystal.

For large interionic distance and no overlapping, E_{elstat} must reduce to the Madelung energy. Let ϵ_g be the valence of the ion on site g, and let $\rho'_g(1)$ be a neutral spherical charge distribution of the ion at site g, such that

$$\rho_g(1) = \rho_g'(1) + \epsilon_g\, \delta(\vec{r}_1, 0) .$$

With these definitions,

$$E_{elstat} = \left(\frac{1}{2N}\right) \sum_{g,g'}{}' \frac{2\epsilon_g\, \epsilon_{g'}}{r_{gg'}} + \left(\frac{1}{2N}\right) \sum_{g,g'}{}' \int \frac{2\rho_g'(1)\, \rho_{g'}'(2)}{r_{12}}\, dv_1\, dv_2 \qquad (8\text{-}20)$$

The first term is directly the Madelung energy, $-2\alpha/a$; α is the Madelung constant (positive by definition), and a is the interionic distance. This term by itself accounts for most of the observed cohesive energy and thus prompts the ionic starting approximation. In the second term of Eq. (8-20), the sum over g can be reduced to N times the sum over the two sites g in a single cell, say cell O. Thus we can write

$$E_{elstat} = E_{mad} + E_{cc}, \qquad (8\text{-}21)$$

where

$$E_{mad} = -\frac{2\alpha}{a} \qquad (8\text{-}22)$$

and

$$E_{cc} = \frac{1}{2} \sum_{g}^{\text{cell O}} \sum_{g' \neq g} \int \frac{2\rho_g'(1)\, \rho_{g'}'(2)}{r_{12}}\, dv_1\, dv_2 \qquad (8\text{-}23)$$

In Eq. (8-23) for E_{cc} $\rho_g'(1)$ and $\rho_{g'}'(2)$ are neutral spherical distributions, and so have no interaction unless the electronic shells penetrate one another. When there is overlap, E_{cc} represents a correction to E_{mad} due to the electronic charge extension; E_{cc} is called the Coulomb correction energy by Löwdin. If the nucleus of no ion is appreciably within the electronic shells of any of its neighbors, then E_{cc} is negative and represents an attraction of the ions for one another.

Exchange Energy

Reducing the sum over g in the second of Eqs. (8-18), the exchange energy is found to be

$$E_{ex} = -\sum_{g}^{\text{cell O}} \sum_{m}^{g} \sum_{p}^{g} (G|mp|pm) . \qquad (8\text{-}24)$$

The exchange energy is therefore the sum over all electrons in a single cell of the exchange interaction between those electron and electrons on other ions. E_{ex} is necessarily negative and implies an attraction of the ions for one another.

E_S

The S-energy, E_S, depends on the coefficients P_{nm} are derived from the in-

verse overlap matrix, Δ^{-1}. Löwdin showed that this matrix Δ^{-1} can often be expanded in a convergent infinite series in S(defined by Eq. (8-10); thus

$$\Delta^{-1} = 1 - S + S^2 - \ldots \quad .$$

when this expansion is valid, the coefficients P_{nm} are given by

$$P_{nm} = - S_{nm} + \sum_p S_{np} S_{pm} - \ldots \quad .$$

If there is no overlap between ions, then all the P_{nm} are zero, and E_S is zero.

To give E_S some meaning let us look at the crystal charge density, $\rho(1)$. In our approximation $\rho(1)$ is given by

$$\rho(1) = 2 \sum_{i=1}^{M} \psi_i^*(1)\, \psi_i(1) = 2 \sum_{m,n} \Delta^{-1}_{nm}\, u_m^*(1)\, u_n(1),$$

or using Eq. (8-13) for Δ^{-1}_{nm},

$$\rho(1) = 2 \sum_{m=1}^{M} u_m^*(1)\, u_m(1) + 2 \sum_{mn} P_{nm}\, u_m^*(1)\, u_n(1) \,. \qquad (8\text{-}25)$$

Thus $\rho(1)$ is made up of a superposition of free ion charge densities, which of course neutralizes the nuclear charges, plus a neutral correction charge density. The correction term removes electronic charge from regions of overlap and adds it to the spherical charge of the ion. For KCl, for example, about 0.2 electron charges are added to the original charge of a free Cl^- ion. This correction charge is a direct result of the exclusion principle and of the principle of the indistinguishability of electrons; these principles led us to use a single determinant rather than a simple product for the crystal wave function.

The S-energy can now be thought of as the self energy of this correction charge density plus its energy of interaction with the charge density arising from the superposition of free ions. Since E_S includes kinetic, coulomb, and exchange terms, the contributions to it are not all of one sign. The overall term must be positive, however, as it represents a shift of charge from the optimum free ion distribution to something more concentrated about the nucleii; a shift of this sort implies that E_S must contain terms which represent an increase in the energy of the "individual ions" as well as terms which reduce the effect of the overlap-dependent, negative quantities, E_{cc} and E_{ex}. Both of these conclusions imply a positive energy term E_S. This S-energy is the only term which opposes binding, therefore, and it is E_S which prevents collapse of the KCl crystal.

For calculational purposes the equation for E_S, the third of Eqs. (8-18), will be rewritten to involve one-electron matrix elements. From a previous Report,[3] these matrix elements are given by the equation

$$H_{mn} = (H|mn) + \sum_{p,q=1}^{M} \Delta_{qp}^{-1} \left[2(G|mn|pq) - (G|mq|pn)\right] . \tag{8-26}$$

Using this, the equation for E_S (Eq. (8-18)) can be written as

$$E_S = \frac{1}{N} \sum_{g} \sum_{m}^{g} \sum_{n} P_{nm} Q_{mn} , \tag{8-27}$$

where

$$Q_{mn} = 2H_{mn} - \sum_{pq} P_{qp} \left[2(G|mn|pq) - (G|mq|pn)\right] .$$

Q_{mn} is easily calculated from the elements H_{mn} and from terms which have been calculated as part of the ingredients of H_{mn}. In Eq. (8-27) the terms for which m and n are on the same site are negative while the others are positive. An alternative form in which all contributions are positive is desirable. By definition,

$$\Delta^{-1}\Delta = 1 = (1 + P)(1 + S) = 1 + P + S + PS , \tag{8-28}$$

or

$$P + S + PS = 0$$

The $(nm)^{th}$ equation of this form is

$$P_{nm} = - S_{nm} - \sum_{p} P_{np} S_{pm} . \tag{8-29}$$

In Eq. (8-27) for E_S we can separate from the sum those terms for which n is on the same site as m. We substitute Eq. (8-29) for P_{nm} in those terms, realizing that here S_{nm} is zero; we interchange orders of certain summations; we change the names of a few indices; and finally we obtain for the S-energy:

$$E_S = \sum_{g}^{\text{cell O}} \sum_{m}^{g} \left\{ \sum_{g' \neq g} \sum_{n}^{g'} P_{nm} \left[Q_{mn} - \sum_{p}^{g'} S_{mp} Q_{pn} \right] \right\} \tag{8-30}$$

In this form all the contributions to E_S are positive and the cancellation of terms in the square brackets becomes more exact as the orbitals involved become more tightly bound. E_S will be calculated from Eq. (8-30).

Calculations

The free-ion orbitals $u_m(j)$ are chosen real, and the radial functions are linear combinations of Slater orbitals fitted to the Hartree-Hartree numerical tables. Löwdin's fit[2] was used for the important Cl^- 3p orbital, and new fits were made for the Cl^- 3s and all K^+ orbitals. The orthonormalized fitted functions reproduced the Hartree-Fock energy parameters of Hartree and Hartree to about the accuracy with which they are given.[4] With these orbitals the one- and two-electron integrals required in Eqs. (8-23), (8-24), (8-26), and (8-30) were calculated by the Barnett-Coulson scheme (as adapted for Whirlwind by F. J. Corbató);[5] in this scheme all the orbitals in an integral are expanded in spherical harmonics about some one center. For the most part only integrals involving the outer shell orbitals (n = 3) were included. Effective nuclear charges for potential for the ions were calculated for use in Eq. (8-23). Important three-center integrals involving 1/r on one center were calculated exactly, while other three- and four-center integrals were estimated. The coefficients P_{nm} were found by using their symmetry properties and solving a set of eighteen simultaneous equations for eighteen Δ_{nm}^{-1}'s given the values of Δ_{nm}. The results for P_{nm} agreed with the first term of a Löwdin power series in S to one figure; and they agreed with a more complete expansion to three or four figures in the few cases tested.

Results

Although E_{cc}, E_{ex} and E_S have been discussed separately above, this separation has little physical significance. Their magnitudes all increase with electronic overlap and go to zero if there is no overlap. E_{cc} and E_{ex} are negative, and the E_S is positive, so there is important cancellation among them. We shall therefore lump the three terms together into a single contribution which we shall call the overlap energy, E_{ov}, after Born and Huang.[6] To summarize our equations and notation, the lattice energy is now given by

$$E = E_{mad} + E_{ov}, \tag{8-31}$$

where

$$E_{ov} = E_{cc} + E_{ex} + E_S; \tag{8-32}$$

here E_{cc} is given by Eq. (8-23), E_{ex} by (8-24), and E_S by (8-18), (8-27), or (8-30).

The results of the present calculation are summarized in row (A) of the following table. The notation in the first column indicates that both chlorine-potassium and chlorine-chlorine interactions were included. The value of the interionic distance a used was 5.9007 a.u. or 3.122 Å, appropriate to KCl at - 180°C (where the V-center experiments are performed). The predominant contribution to E is the negative Madelung energy; the overlap energy provides a ten percent positive correction to this.

Table 8-1

Crystal energy of KCl: Summary of results in kilocalories/mole

Source	E_{mad}	E_{cc}	E_{ex}	E_S	E_{ov}	$E = E_{mad} + E_{ov}$	U
A) H(Cl, K + Cl, Cl)	-185.8	-21.0	-60.1	+106.6	+25.5	-160.3	
B) H(Cl, K)	-185.8	-17.7	-49.6	(+ 89.3)	(+22.0)		
C) Löwdin (Cl, K)	-185.8	-16.5	-48.6	+ 84.0	+18.9	-166.9	
D) A - C (Cl, Cl)					+ 6.5		
E) Huggins	-185.8				+23.2	-162.6	-167.9
F) Exp. (Born-Mayer)							-167.8 ± 2

It is simple to obtain the partial values of E_{cc} and E_{ex}, calculated on Löwdin's assumption that there is no appreciable chlorine-chlorine overlap; the results are shown in row (B) of Table 8-1. It is not possible to find the value of E_S appropriate to Löwdin's assumption, however, unless both H_{mn} and P_{mn} are redetermined (Eq. (8-31)). It is possible to obtain something close to Löwdin's E_S, however, by extending the summations of Eq. (8-31) only over pairs (n, m) which correspond to potassium-chlorine pairs. Such an approximate value is shown in parenthesis in row (B) of Table 8-1; a value of E_{ov} calculated from this approximate E_S is also shown in parenthesis.

Löwdin's results are shown in row (C) for comparison with the results of row (B). The values of E_{cc} and E_{ex} seem to compare fairly well between rows; the two rows should be the same, of course, if the orbitals used are identical in the two calculations. Only the Cl^- 3p orbitals are identical, however, and the interactions of my analytic K^+ functions with the Cl^- functions might be expected to be larger in magnitude due to the longer tails. The approximate E_S of row (B) is in qualitative agreement with Löwdin's value. The general agreement between rows (B) and (C), then, along with other consistency checks, is taken as providing a fairly good check on the quantities used here and to be used in the electronic structure calculations.

The contribution of the Cl, Cl interaction to lattice energy is approximately the difference between my results (row A) and Löwdin's (row C); this would be exactly true if the orbitals used were the same. In Löwdin's approximation the overlap energy is 18.9 kcal/mole; then the Cl, Cl interaction contributes another 6.5 kcal/mole (row D) to this and hence to the lattice energy. Further interactions involving inner shell electrons or electrons on more distant neighbors may add another one or two kcal/mole to the values of E_{ov} and E in row (A), but probably not more than that. Computational errors probably provide an additional uncertainty in E_{ov} and E of about one kcal/mole. The value of E in row (A) is therefore probably within two or three kcal/mole of the

correct value based on the wave function assumed.

A comparison of the foregoing results with experiment will be made via theoretical analysis based on the Born-Mayer model. The most up-to-date refinements of the latter work were made by M. L. Huggins.[7] In that work the lattice energy of an NaCl-type lattice was taken to be (in C.G.S. units)

$$U = \left[-\frac{\alpha e^2}{a}\right] + \left[-\frac{C}{a^6} - \frac{D}{a^8}\right] + \left[+\frac{9}{4}h\nu_{max}\right] + \left[b\,6\,e^{\lambda(r_+ + r_- - a)} + b\,4.5\,e^{\lambda(2r_- - \sqrt{2}a)} + b\,7.5\,e^{\lambda(2r_+ - \sqrt{2}a)}\right], \tag{8-33}$$

where U is regarded as a function of the interionic distance a. The first bracketed term in Eq. (8-33) is the Madelung energy, and α is the same constant which appears in (8-22). The second bracketed term contains the contributions of van der Waals' or dipole-dipole interactions between the ions and of dipole-quadrupole interactions; the constants C and D were determined by Mayer using crystal spectroscopic data. The third bracketed term in Eq. (8-33) is the zero-point energy of the lattice, ν_{max} being a Debye cutoff frequency. The last bracketed term contains three quantities, the first representing repulsion between nearest positive and negative ions, the second between nearest negative ions, and the third between nearest positive ions. The constants b, λ, r_+, and r_- are undetermined; $a\sqrt{2}$ in the exponents of the last two terms is the second neighbor separation; and the numerical coefficients were determined by rules of Pauling.

In his calculation, Huggins chooses an arbitrary value for b. He uses a value of λ calculated by Born and Mayer, who fitted compressibility and equilibrium-distance data, and who averaged λ over all alkali halides. He then obtains a set of "ionic radii" r_+ and r_- to predict accurate interionic distances. With these radii he recomputes λ and performs another cycle. The process leads to a lattice energy U which is the energy of the lattice at 0°K relative to the energy of the separated ions at 0°K. His result, given in the last column of row (E) of Table 8-1 agrees with the experimental value obtained by the Born-Haber cycle (row F) to within 0.1 kcal/mole, though the uncertainty in the latter is about 2 kcal/mole.

What has been called E in the present work is not the same thing as Huggins' U. To obtain something comparable to U the zero-point energy of the lattice should be added to E and my interionic distance a should be the 0°K value. Both these effects are small. The important difference between U and E is that the former explicitly includes the dipole-dipole and dipole-quadrupole interactions between electrons on different ions in the lattice. These effects imply a correlation of the motion of electrons on different ions. A single determinant wave function provides no possibility for such

correlation, except in a limited way through exchange correlation. Only by configuration interaction, using our single determinant ψ as a leading term, can we obtain the necessary correlation effects.

If our starting determinant (Eq. (8-1)) were the best possible (determined by a Hartree-Fock procedure), then separate configuration interactions for the crystal and for the separated ions should lead to a correction to E which is roughly given by the empirical van der Waals terms in Eq. (8-33). The correlation effects within any ion should cancel out in the process of subtracting E_∞ from E_T. Since our starting determinant is not the best possible, the configuration interactions must also correct for deficiencies in the one-electron orbitals and yield a larger correction to E than the empirical van der Waals terms would predict. On the basis of these remarks it would appear that if our single determinant is the best, then the value of E_{ov} obtained from it should agree with the repulsion terms calculated by Huggins (the last bracketed terms in Eq. (8-33)), since Huggins' overall result agrees so well with experiment. Because our determinant is not the best, E_{ov} should be larger than the Huggins repulsion, leading to too high a crystal energy.

The Huggins repulsion terms were recalculated using his constants, but my value of the interionic distance a; the result appears in row (E) of Table 8-1 under the heading E_{ov}. E_{mad} in this row is of course the same as in all other rows. The value of E_{ov} in row (A) is larger than the Huggins repulsion by about ten percent, consistent with the discussion of the preceding paragraph. From our earlier discussion this difference might increase to fifteen percent if further neighbors were included in the calculation. According to Löwdin's results, however, the calculated value of E_{ov} is substantially less than the Huggins repulsion; in fact his value of E is almost as low as U itself, and it leaves no room for the correlation effects which must occur. Inclusion of the second neighbor Cl, Cl interactions has therefore removed an apparent anomoly of the quantum mechanical calculation.

The comparisons above appear to justify roughly the starting approximation of using a single determinant of free-ion orbitals for the crystal wave function. In regions midway between ions this wave function and the charge density it predicts cannot be too good, but the correction charge which it introduces (Eq. (8-25)) does modify the charge of superposed free ions in the right direction. Small errors in the wave function do not appreciably affect the energy value, of course, and our value for the lattice energy profits from this insensitivity.

Several interesting facts were uncovered in analyzing Huggins' calculation. Our equations for contributions to E_{ov} suggest that E_{ov} might vary with interionic distance as the square of some critical overlap or overlaps. An overlap integral between orbitals on two separated ions varies exponentially with r unless r is too small. A function $A_{+-}e^{\lambda_{+-}r}$ was therefore fitted to a curve of the square of the largest Cl, K

overlap integral versus r, and a value for λ_{+-} of 3.6 per Å was found. Another function $A_{--}\, e^{\lambda_{--} r}$ was fitted for the largest Cl, Cl overlap, and a value for λ_{--} of 2.8 per Å was found. The value which Huggins determined for λ in Eq. (8-33), on the other hand, was 3.00 per Å. Thus Huggins' λ is a mean between values expected from variation of these largest overlap integrals.

A further point is that the Huggins value for E_{ov}, 23.2 kcal/mole, is made up of three contributions, 22.26 for the +- term, 0.63 for the -- term, and 0.32 for the ++ term. The present calculation indicates that the relative contributions of Huggins' +- term and his -- term is far from representing the relative contributions of Cl, K and Cl, Cl interactions. The fact that λ is a mean between λ_{+-} and λ_{--} (preceding paragraph), rather than being much nearer λ_{+-}, again indicates that the +- term must be including a large part of the Cl, Cl contribution. This fact may well be responsible for the errors Huggins finds in values of the compressibility and of the maximum optical frequency which he obtains from his equation for U.

References

1. L. P. Howland, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., July 15, 1955, p. 15.
2. P. O. Löwdin, Ph.D. Thesis, Uppsala (1948).
3. L. P. Howland, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., October 15, 1955, p. 28.
4. L. P. Howland, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., January 15, 1956, p. 38.
5. F. J. Corbató, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., April 15, 1955, p. 44.
6. M. Born and K. Huang, Dynamical Theory of Crystal Lattices, Clarendon Press (Oxford) 1954, Chapter I.
7. M. L. Huggins, J. Chem. Phys. 5, 143 (1937).

L. P. Howland

9. CALCULATIONS ON ATOMIC IRON

In writing up the results of this calculation, we have included the one-electron wave functions, one-electron energy parameters, total charge density for electrons of each spin total potential function, and the components of all the coulomb and exchange integrals (not, as yet, kinetic energy). Although it is expected to include these quantities in the published paper, any and all are currently available from the writer.

The behavior of the radii as a function of distance from the nucleus were determined from the charge densities of each spin, ρ_+ and ρ_-. The size of these radii are a measure of the applicability of the particular approximation[1] employed in the calculation.

Let us consider a particular orbital u_i describing an electron of plus spin. Then, as described in the reference, the potential entering into the Hartree-Fock equation for this orbital is constructed from the total charge density $(\rho_+ + \rho_-)$ and an additional charge distribution, the so-called "Fermi" or "exchange hole". This exchange hole corrects the distribution of charge in the immediate vicinity of the electron occupying u_i by subtracting from ρ_+ (in this case) a quantity of charge equivalent to one electronic charge. The density of this quantity of charge falls off as we move away from the position of the electron and the calculation of this density for the free-electron case[1] shows that it falls to small values a distance r_o away where

$$\frac{4}{3}\pi r_o^3 |\rho_+| = e$$

which would give the radius of this exchange hole if the exchange charge density were uniform and occupied a sphere just large enough to correspond to removal of one electronic charge.

One of the limitations on the use of the free-electron approximation used in this calculation for treating exchange is the requirement that the potential in which an electron moves be essentially constant over the exchange hole. Since the quantities ρ_+ and ρ_- were available, the radii of the exchange holes for plus and minus spin, as defined above, can be and were found as a function of distance from the origin. Considering first the radius of the plus spin exchange hole, we find that it has small values near the origin (.045 atomic units at .02 a.u. from the nucleus) and increases in a roughly linear fashion with a slope of about 1. The radius for the minus spin hole follows much the same behavior but is on the average 0.3 a.u. greater than the corresponding radius of the plus spin hole.

The larger radius for minus spin is a reflection of the fact that we have four fewer electrons of minus spin in our particular configuration. The radii are

somewhat larger than one might hope if the potential were to be constant over the hole.

Reference

1. J. C. Slater, Phys. Rev. 81, 384 (1951); also G. W. Pratt, Jr., Phys. Rev. 88, 1217 (1952).

J. H. Wood

10. AN AUGMENTED PLANE WAVE METHOD AS APPLIED TO SODIUM AND CHROMIUM

Testing of the matrix element generation routine is still going on. It appears, however, that production work will soon begin. In the course of testing it was found that the normalization constant for the radial wave functions for angular momentum greater than eight were negative. The error was traced to a program which, I believe, was used by Howarth in his calculation on copper. However, the error was easily corrected. The corrected version is now being used until a completely new and recently written program for the calculation of overlap and ratio of slope to function for the radial components of APW is tested.

Work on chromium has been halted until a better potential than has been used can be obtained. It is planned to use potentials obtained by Nesbet's routines for atoms.

M. M. Saffren

11. DESCRIPTION OF MANY-ELECTRON SYSTEMS BY TWO-PARTICLE ORBITALS

I have described in previous reports[1] the application of my Coulomb hole short-range correlation correction to two-electron systems, and the way in which two-particle orbitals so obtained may be combined to form N-electron wave functions. In this Report, I shall mention some simplifications of the procedure, and the types of integrals which must be evaluated in calculations on systems described by such wave functions.

Considering a system which may be described in the orbital approximation by a single determinant Φ of orthonormal spin-orbitals $\psi_k(i)$, the corrected wave function is

$$\Psi(1, 2 \ldots N) = \Phi(1, 2 \ldots N) \left\{1 + \sum_{i<j} f'(i, j)\right\} \tag{11-1}$$

where $f'(i, j)$ are correction functions, each confined to the particular region where r_{ij} is small -- the first restriction being that regions where more than one of the r_{ij} are small are arbitrarily excluded. By the strict derivation of the Coulomb hole correction, the two-electron function $f'(i, j)$ and the radius $S(i, j)$ of the correction sphere should depend on the positions and spins of the other N - 2 electrons; the second restriction is to neglect this, and take $f'(i, j)$ and $S(i, j)$ as being of the same form for all pairs, whether singlet or triplet pairs, regardless of the effect of the other N - 2 electrons. It is by these two simplifying restrictions that we can use the form (11-1) for the N-electron wave function; it is also thanks to these restrictions that all properties of the corrected wave function can be calculated in terms of a few basic integrals, common to all systems of the same symmetry. The relation of $f'(i, j)$ to the $f(i, j)$ used before[1] is simply that $f'(i, j) = f(i, j) - 1$, so that $f'(i, j)$ is zero outside the correction region. I further define $G(i, j) = \left[f(i, j)\right]^2 - 1$, which performs exactly the same role in the expansion of Ψ^2 or of $\Psi_m^* \Psi_n$ as does $f'(i, j)$ in the expansion of Ψ in (11-1), so that

$$\Psi_m^* \Psi_n = \Phi_m^* \Phi_n \left\{1 + \sum_{i<j} G(i, j)\right\} \tag{11-2}$$

Using this expansion, the diagonal density matrices (using the terminology of Löwdin[2]) for the corrected N-electron wave function can be expressed in terms of the density matrices for the uncorrected Φ and the following quantities:

$$\begin{aligned} \xi_{ab, cd}(i, j) &= \psi_a^*(i)\, \psi_b(i)\, \psi_c^*(j)\, \psi_d(j)\, G(i, j) \\ \eta_{ab, cd}(i) &= \int_{r_{ij} < 2S_{ij}} \xi_{ab, cd}(i, j)\, d\tau_j \\ \zeta_{ab, cd} &= \int_{r_{ij} < 2S_{ij}} \eta_{ab, cd}(i)\, d\tau_i = \int_{r_{ij} < S_{ij}} \xi_{ab, cd}(i, j)\, d\tau_i\, d\tau_j \end{aligned} \tag{11-3}$$

the integrals being taken only over the corrected region. The expressions for the density matrices are obtained straightforwardly by methods like those usually used in obtaining matrix elements between determinantal wave functions;[2] for instance, the normalization integral is

$$\int \Psi^* \Psi \, d\tau_1 \cdots d\tau_N = \int \Phi^* \Phi \, d\tau_1 \cdots d\tau_N + 2 \sum_{k<l} \left\{ \zeta_{kk,ll} - \zeta_{kl,lk} \right\} \qquad (11\text{-}4)$$

When the average value of a one-electron operator Ω_1 is to be computed, two-electron integrals over the correction functions are needed

$$\Delta\Omega_1(ab|cd) = \int_{r_{12}<2S_{12}} \psi_a^*(1)\psi_c^*(2)\psi_d(2) \left\{ f(12)\,\Omega_1\,\psi_b(1) f(12) - \Omega_1 \psi_b(1) \right\} d\tau_1 \, d\tau_2 \qquad (11\text{-}5)$$

For two-electron operators, Ω_{12}, unfortunately including the electron repulsion operator in the Hamiltonian, three-electron correction integrals are needed:

$$\Delta\Omega_{12}(ab|cd|ef) = \int_{r_{13}<2S_{13}} \psi_a^*(1)\psi_c^*(2)\psi_e^*(3)\psi_f(3) \left\{ f(13)\,\Omega_{12}\,\psi_b(1)\psi_d(2) f(13) - \Omega_{12}\psi_b(1)\psi_d(2) \right\} d\tau_1 \, d\tau_2 \, d\tau_3 \qquad (11\text{-}6)$$

I am now writing programs to compute the one- and two-electron integrals like (11-3) and (11-5) for the case of spherical symmetry -- that is, for the He atom, the same integrals with changed parameters being applicable to any atom. The case of atoms not in S states can be handled by the same programs by the device of introducing an angular part of the correction function f(i, j) so that the total corrected wave function in the corrected region is made independent of the direction of the interelectron vector -- the essential dependence on the magnitude r_{ij} thus not being affected.

The three-electron integrals like (11-6) are not yet being attempted! Computational difficulty for a one-center, three-electron integral is comparable with that for a two-center, two-electron integral.

References

1. J. Hawgood, Quarterly Progress Report, Solid-State and Molecular Theory Group M. I. T., October 15, 1955, January 15, 1956, and April 15, 1956.

2. P. O. Löwdin, Phys. Rev. 97, 1474 (1955).

J. Hawgood

12. ON THE POLARON ENERGY AND MASS

R. P. Feynman[1] in his approach to the polaron problem has compared the problem of an electron interacting with the phonon field with that of an electron interacting harmonically with a second particle of arbitrary mass. He has achieved a variational expression for the ground state energy of the first problem in terms of the two variable parameters of the second, the mass M of the second particle and the spring constant k of the harmonic coupling. Rather than these two parameters, Feynman introduces the parameters v and w related to M and k by

$$w = \sqrt{k/M} \text{ and } v = \sqrt{k(1 + 1/M)} \tag{12-1}$$

In terms of these parameters, an upper bound to the energy is given by

$$E_F(v_1, w) = \frac{3}{4v}(v - w)^2 - \frac{\alpha v}{\sqrt{\pi}} \int_0^\infty \frac{e^{-t}\, dt}{\sqrt{w^2 t + \frac{v^2 - w^2}{v}(1 - e^{-vt})}} \text{ (units of } \hbar\omega) \tag{12-2}$$

which is to be minimized with respect to v and w. For the best choice of v and w an estimate of the effective polaron mass for very slow polarons is given by

$$m_F = 1 + \frac{\alpha v^3}{3\sqrt{\pi}} \int_0^\infty \frac{e^{-t}\, t^2\, dt}{\sqrt{w^2 t + \frac{v^2 - w^2}{v}(1 - e^{-vt})}} \tag{12-3}$$

Feynman obtains the latter expression by making what amounts to a kind of first order correction to the total mass of the approximating two particle system, $m_T = M + 1 = v^2/w^2$. Feynman also has given approximate expansions for v, w, E_F, and m_F in the weak and strong coupling limits. Because of the conflicting estimates[2] of the polaron mass in the coupling range $\alpha = 5 - 7$, it was felt advisable to carry out the minimization of (12-1) and the determination of the mass to zero order, m_T, and to first order, m_F, comparing these with each other and with masses calculated by other methods.

The repeated evaluation of (12-1) for many values of the pair (v, w) was performed by the Whirlwind computer. Any program for the evaluation of these integrals had to contend with the singular behavior of the denominator for $t \to 0$, the rapidly changing factor e^{-vt} in the denominator, and the infinite range of integration. The program finally developed treated the range in two parts, from zero to t_o and from t_o to ∞, where $t_o = 7.5/v$. In the first region the variable transformation $y^2 = t/t_o$ removes the singularity at the origin, includes all the range of troublesome behavior of e^{-vt} in a way independent of v, and allows accurate integration with 16-point Gauss-Legendre quadratures.[3] In the second region the variable transformation $y = t - t_o$ allows accurate integration with 15-point Gauss-Leguerre quadratures.[4] Since the

energy is very insensitive to the choice of v and w, six-place accuracy in computing (12-1) was required. This was achieved in a computer code written by Miss Hannah Paul requiring between one and two seconds per integral. Subsequent minimization of E(v, w) was carried out graphically by Miss Paul.

In Table 12-1 we have listed the values of v, w, E_F, m_T, and m_F found for various values of α. For comparison we have also listed the energy ($E_{LLP} = -\alpha$) and mass ($m_{LLP} = 1 + \alpha/6$) found by Lee, Low and Pines and Gurari,[5] the mass($m_{Ha} = \frac{1+\alpha_{12}}{1-\alpha_{12}}$) found by Haga[6] based on the LLP procedure, the energy we have computed using Gross's transformation superposed on the LLP shift function,[7] and the energy ($E_{PBT} = -.1088\alpha^2 - 3/2$) and mass ($m_{PBT} = 232(\alpha/10)^4$) obtained by Pekar,[8] Bogolyubov,[9] and Tyablikov.[10] It should be noted that the Pekar energy expression is not derived from a variational calculation so that it may be lower than the true energy. It is true that Tyablikov[11] and Höhler have derived this expression variationally but only in the limit of very large coupling.

What is immediately noticed is that the Feynman energy is significantly lower (hence better) in the coupling region of interest than the energy from any other theory and that the Feynman masses M_T and M_F differ considerable from both the LLP and PTB values in this range of α. Furthermore, the behavior of Haga's expression for $\alpha \to 12$ is again seen to be objectionable.

In addition to the fact, shown by Feynman, that m_F has essentially the right behavior in both the weak and strong coupling limits,* we now have the encouraging information that m_F makes only a small correction to the simpler m_T at all coupling strengths. Thus, a theory of mobility, for example, which contains implicitly the approximation of m_T for the polaron mass should not be so much in error. Theories using m_{LLP} or m_{PBT} may be considerably in error if only because of an incorrect description of the slow polaron.

References

1. R. P. Feynman, Phys. Rev. 97, 660 (1955).
2. T. D. Schultz, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., October 15, 1955, p. 43.
3. A. N. Lowan, N. Davids, A. Levinson, Bull. Am. Math. Soc. 48, 739 (1942).
4. H. E. Salzer and R. Zucker, Bull. Am. Math. Soc. 55, 1004 (1949).
5. T-D. Lee, F. E. Low, and D. Pines, Phys. Rev. 90, 297 (1953); M. Gurari, Phil. Mag. 44, 329 (1953).
6. E. Haga, Prog. Theor. Phys. (Japan) 13, 555 (1955).

- - - - - - - - - - - - - - -

*The small constant percentage error occurring as $\alpha \to \infty$ is due essentially to the restricted shape of the effective potential well required by the harmonic approximation.

Table 12-1

Feynman parameters and comparison with other theories

α	$\to 0$	3	5	7	9	11	$\to \infty$
v	$3 + .222\alpha + \ldots$	3.4	4.02	5.81	9.85	15.5	$\sim 4\alpha^2/9\pi - 1.77$
w	$3.00 - O(\alpha^2)$	2.55	2.13	1.60	1.28	1.15	~ 1
E_F	$-\alpha - .0123\alpha^2 + \ldots$	-3.1333	-5.4401	- 8.1127	-11.486	- 15.710	$\sim -.106\alpha^2 - 2.83$
E_{LLP}	$-\alpha$	-3.0000	-5.0000	- 7.0000	- 9.0000		
$E_{G,LLP}$	$-\alpha - .0126\alpha^2 + \ldots$	-3.1	-5.24	- 7.41	- 9.27		
E_{PBT}				- 6.83	-10.31	- 14.7	$\sim -.1088\alpha^2 - 3/2$
m_T	$1 + .148\alpha + \ldots$	1.78	3.56	13.2	59.2	181.	$\sim 202(\alpha/10)^4$
m_F	$1 + .167\alpha + \ldots$	1.89	3.89	14.4	62.8	185.	$\sim 202(\alpha/10)^4$
m_{LLP}	$1 + .167\alpha + \ldots$	1.50	1.83	2.17			
m_{Ha}	$1 + .167\alpha + \ldots$	1.67	2.43	3.80	7.00	23.00	$\to \infty$ at $\alpha = 12$
m_{PBT}			14.5	55.7	152.	340.	$\sim 232(\alpha/10)^4$

References (con'd)

7. E. P. Gross, Phys. Rev. 100, 1571 (1955)
8. S. I. Pekar, Untersuchungen über die Elektronentheorie der Kristalle, Akademie Verlag, Berlin (1954) p. 75 and p. 51 (translated from the Russian edition published in 1951).
9. N. N. Bogolyubov, Ukr. Mat. Zh. 2, 3 (1950).
10. S. V. Tyablikov, Zh. Eksp. Teor. Fiz. 21, 377 (1951).
11. S. V. Tyablikov, Zh. Eksp. Teor. Fiz. 25, 688 (1953).
12. G. Höhler, Z. Physik 140, 192 (1955); Il Nuovo Cimento 2, 691 (1955)

T. D. Schultz

13. ON THE MOBILITY OF THE POLARON

The simplest property of the polaron which one has attempted to observe experimentally is not the self energy or effective mass of a slow polaron but the polaron mobility. Attempts have been made to calculate the electron mobility in polar crystals including some treatment of self energy and mass corrections by Fröhlich, Pelzer and Zienau,[1] Low and Pines,[2] Morita et al.,[3] Pekar[4] and the author.[5] Characteristic of these approaches has been the attempt to base the mobility calculation on standard transport theory applied to a more subtle description of the polaron than calling it a bare electron. More direct attempts to calculate the mobility without a detailed calculation of free polaron properties or a specific reliance on the Boltzmann equation have been made by Lax[6] and Feynman,[7] although these have not yet provided results comparable to the earlier works. Of these more complete analyses, only that of Morita et al. does not rest on one particular description of the polaron, and those of FPZ, LP, and Pekar depend on descriptions which seem inferior to the Feynman approach (see preceding Report). It has therefore been our aim to apply the Feynman description of the polaron to the mobility problem. An approximate application of this technique has been achieved and will be described in detail in the author's doctoral dissertation and eventually in the literature. We shall restrict ourselves here to summarizing a few salient features.

(1) The phonon-polaron scattering problem is best considered as a resonance scattering problem for two reasons. First, it avoids the necessity for a description of the motion of a "fast" polaron, i. e. one which has absorbed a phonon and so can emit one spontaneously. Such a polaron is not even approximately in a stationary state in most cases, and cannot be described in the same way as a polaron with small but non-zero momentum. Second, it avoids the difficulties discussed by Howarth and Sondheimer[8] in solving the Boltzmann equation when the simple scattering process produces a significant change in the particle energy.

(2) It may well be that the resonance scattering can be considered as that of a field quantum by a quasi-particle, but even if this is so one must know not only the energy-momentum relation for the particle near zero momentum, but also the resonance momentum and velocity (calculated from knowing the energy-momentum relation well away from zero momentum) and the width of the intermediate (resonance) state. In this respect the assumptions of FPZ and of Pekar prove unacceptable.

(3) There is evidence from LP's work that the resonance scattering cannot be considered simply as that of a field quantum by a quasi-particle as manifested in the $(m/m^*)^3$ rather than $(m/m^*)^{3/2}$ dependence of mobility on polaron mass found in their paper. The analysis of Morita et al. however suggests to the contrary.

(4) The simple replacement, described in a previous Report,[5] of the exact effective action for the electron propagation by the approximate action introduced by Feynman is unsatisfactory in one important respect. Since the effective action describes

the motion of one particle in a two-particle system having only bound states, it is incapable of giving a finite width to the polaron state after absorption of a phonon. Since this width is crucial in obtaining a finite resonance scattering probability, the results previously reported are, as they stand, meaningless. Furthermore, any finite order correction to the use of the simple approximate action obtained by summing over a finite number of Feynman diagrams with virtual phonons representing the difference between the approximate and exact effective actions cannot give a finite width to this intermediate state just as no finite order of perturbation theory could give the Weisskopf resonance fluorescence formula in light scattering by atoms.

(5) A special but infinite set of Feynman diagrams can be summed over in this case with good approximation and a width is obtained. These calculations are best performed by proving the equivalence of the Feynman formulation of the polaron problem with an extended Hamiltonian formulation and then doing the sums in the Hamiltonian formulation. One finds that the picture of resonance scattering as that of a field quantum by a quasi-particle is valid, at least to this approximation, contrary to the results of Low and Pines, and in agreement with Morita et al. That is, the mobility depends on the polaron mass as $(m/m^*)^{3/2}$. One also finds that if similar corrections are calculated for the slow motion of a free polaron, the effective mass is changed by only a few percent from m_T or m_F discussed in the previous Report.

References

1. H. Fröhlich, H. Pelzer, and S. Zienau, Phil. Mag. 41, 221 (1950).
2. F. E. Low and D. Pines, Phys. Rev. 91, 193 (1953) and Phys. Rev. 98, 414 (1955) hereinafter referred to as LP.
3. A. Morita, Science Reports of the Tohoku University, (I) XXXVIII, 1 (1954) and A. Morita, C. Horie and K. Hasegawa, Sci. Rpts. of Tohoku U., (I) XXXVIII, 157 (1954) hereinafter referred to as Morita et al.
4. S. I. Pekar, Untersuchungen über die Elektronentheorie der Kristalle, Akademie Verlag, Berlin (1954), pp. 79ff. (translated from the Russian edition published in 1951). For additional objections to this treatment, see the unpublished Technical Report No. 2, The Motion of Slow Electrons in a Polar Crystal, pp. 23ff. by Yako Yafet, University of Illinois.
5. T. D. Schultz, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., October 15, 1955, p. 41 and Bull. Am. Phys. Soc. II, 1, 25 (1956).
6. M. Lax, Bull. Am. Phys. Soc. I, 30, 24 (1955).
7. R. P. Feynman, private communication. We are indebted to Professor Feynman for his correspondence and valuable suggestions.
8. D. J. Howarth and E. H. Sondheimer, Proc. Roy. Soc. A209, 53 (1953).

T. D. Schultz